EFFECT OF DIFFUSION AND ADSORPTION ON SELECTIVITY OF SOME COMPLEX REACTIONS

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ABSTRACT

The effect of diffusion limitation on selectivity of some complex reactions in a cylindrical catalyst pore has been studied using Langmuir-Hinshelwood type of rate expressions which takes into account the effect of adsorption on rate of reactions. All three types of complex reactions, viz. independent, parallel and series reactions have been studied and the results are presented in the form of selectivity ratio as a function of modified Thiele parameter. For each type of reactions only one of the two reactions is considered reversible. The dimensionless parameters studied are: modified Thiele parameter, $\emptyset_M$, equilibrium constant for reversible reaction, K_1, ratio of reaction rate constants, K_2, $K_A p_o$, diffusivity ratios and adsorption equilibrium constant ratios with respect to reactant

Diffusion with chemical reaction results in a set of non-linear differential equations of the boundary value type. A new technique requiring much less computation time is develope to obtain the missing initial conditions of the boundary value problem using the principle of invariant imbedding.

The product distribution as indicated by selectivity ratio is markedly effected by diffusion limitations. The modif Thiele parameter is one of the main variable influencing the value of selectivity ratio. For values of $\emptyset_M$ less than 0.2, the effect is found to be insignificant and at values of $\emptyset_M$ larger than five, the selectivity ratio attains a constant value. Except in two cases for independent reactions, selectivity ratio decreases with increase in $\emptyset_M$. The other variables which have a significant effect on selectivity ratio are K_1, K_2, D_B/D_A, D_E/D_A and $K_A p_o$. Adsorption equilibrium constants and diffusivities of other reaction products are observed to have very small effect.

CERTIFICATE

Certified that the work contained in this thesis has been carried out under my supervision and that the work has not been submitted elsewhere for a degree.
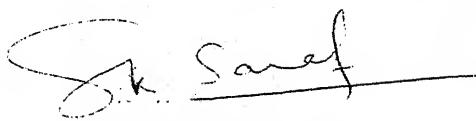
(S.K. Saraf)

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The author would also like to express his gratitude to all who have helped in bringing out this manuscript and finally to my wife for her patience during the preparation of this manuscript.

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LIST OF SYMBOLS

<u>Roman Letters</u>

a   Constant

a   Starting value of the independent variable in the differential equations

A   Component A

A_1, A_2 Constants

$\overline{A}$ Matrix A

b   Constant

B   Component B

B_1, B_2 Constants

$\overline{B}$ Matrix B

c   Initial value of the dependent variable in the differential equations

C   Component C

C   Concentration of the reacting species, moles/cc

C_1, C_2 Constants

d   Initial value of the dependent variable in the differential equations

D   Component D

D   Diffusivity, cm^2/sec.

E   Component E

f   Some function

F   Function of x and y

g   Some function

G   Function of x and y

k_1, k_2 Forward reaction velocity constants for reaction 1 and 2

k_1' Reverse reaction velocity constant for reaction 1

K Adsorption equilibrium constant

K_1 Equilibrium constant for reversible reaction

K_2 Ratio of reaction velocity constants

L Length of the pore

N Number of intervals

p Partial pressure

p_0 Total pressure outside the pore mouth

r Rate of reaction, moles/(unit volume of the catalyst pore)(sec.)

r Some function

R Universal Gas constant

s Some function

S Cross sectional area of the pore

S_0 Selectivity without diffusion effects

S_D Selectivity with diffusion effects

S_R Selectivity ratio, S_D/S_0

t Independent variable of the differential equations

T Temperature

V Constant

$\bar{V}$ Vector V

W Constant

$\bar{W}$ Vector W

x   Dependent variable of the differential equations

$\bar{x}_{n+1}$ Vector x_{n+1}

y   Dependent variable of the differential equations

$\bar{y}_{n+1}$ Vector y_{n+1}

z   Distance along the pore

Greek Letters

α Constant of the rate equations under given conditions

β Constant of the rate equations under given conditions

γ Constant of the rate equations under given conditions

δ Constant of the rate equations under given conditions

ω Constant of the rate equations under given conditions

φ Dimensionless partial pressure, p/p_o

η Dimensionless distance along the pore, z/L

$\emptyset$ Ordinary Thiele parameter

$\emptyset_M$ Modified Thiele parameter

Δ Increment in independent variable

Subscripts (except as noted above)

A   Component A

B   Component B

C   Component C

D   Component D

E   Component E

k   Position variable of independent variable t

n   Number of iteration

0   Condition at the pore mouth

SYNOPSIS

"Effect of Diffusion and Adsorption on Selectivity of some Complex Reactions". A thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy by Avadh Behari Lal Agarwal to the Department of Chemical Engineering Indian Institute of Technology, Kanpur on October 1969.

The effect of diffusion on the selectivity of some complex reactions in a cylindrical catalyst pore has been studied using Langmuir-Hinshelwood type of rate expressions which take into account the effect of adsorption on rate of reactions. The following three types of complex reactions

1. Independent $\quad A \rightleftharpoons B + C$
$\quad E \longrightarrow D + C \quad$ Selectivity $= \dfrac{r_B}{r_D} = \dfrac{-r_A}{-r_E}$

2. Parallel $\quad 2A \rightleftharpoons B + C$
$\quad A \longrightarrow D + C \quad$ Selectivity $= \dfrac{r_B}{-r_A}$

3. Series $\quad A \rightleftharpoons B + C$
$\quad B \longrightarrow D + C \quad$ Selectivity $= \dfrac{r_B}{-r_A}$
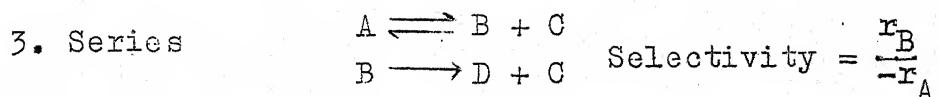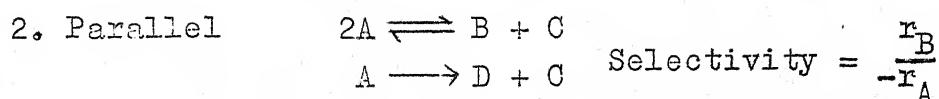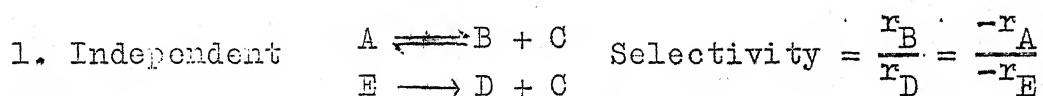
are studied and the results are presented in the form of selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M. The term selectivity ratio is defined as the ratio of selectivity with and without diffusion effects. Modified Thiele parameter is defined as $L\sqrt{\dfrac{k_1 K_A RT}{D_A(1+K_A p_o)}}$.

For each type of complex reactions only one of the two reactions is considered reversible. The dimensionless parameters and the range of their values (given in bracket) studied are: modified Thiele parameter ϕ_M (0.1 - 10.0), reaction

equilibrium constant $K_1(0.1 - 100.0)$, ratio of reaction rate
constant for two reactions $K_2(0.1 - 10.0)$, $K_A p_0(0.01 - 100.0)$,
ratio of diffusivities for component B, C, D and E with respect
to that of reactant A (0.25 - 4.0) and ratio of adsorption
equilibrium constants for component B,C, D and E with respect
to reactant A (0.25 - 4.0). At a time only one variable is
varied while keeping all other variables at a constant value
of unity.

Diffusion with chemical reaction give rise to a set of
non-linear differential equations of the boundary value type.
A new numerical technique is developed to obtain the missing
initial conditions of the boundary value problem using the
principle of invariant imbedding. The missing initial conditions
are required in the present work as they are proportional to the
overall reaction rates in the catalyst pore. This new technique
is simple and takes only 3 seconds on IBM 7044 computer to
obtain the two missing initial conditions for a given set of
variables. Accurate estimation of the value of selectivity
ratio by invariant imbedding technique is possible for values of
modified Thiele parameter up to two, but for larger values,
the results obtained by this technique are in error, because the
increment used is not sufficiently small. Quasilinearization
technique is used to calculate the values of selectivity ratio
for larger values of ϕ_M, upto ten. But this technique also

fails in many cases, especially for series reactions, for $\emptyset_M$ values larger than three. Computer time required by quasilinea_ zation technique to solve these equations for one set of variables varies from 15 to 60 seconds depending on the type of reactions and the values of the coefficients.

The result shows that selectivity ratio of a complex reaction is significantly effected due to diffusion limitation in a catalyst pore. The magnitude depends upon the type of reaction, reaction mechanism and the physical and chemical constants influencing the system. The effect of different variables investigated are as follows:

The selectivity ratio is found to decrease, except for two cases, with increase in modified Thiele parameter upto a value of five. Further increase in $\emptyset_M$ does not effect selectivity ratio. Only for the values of D_E/D_A or K_2 less than unity, the selectivity ratio is found to increase with increase in $\emptyset_M$ in the case of independent reactions. For values of modified Thiele parameter less than 0.2, diffusion limitations are insignificant and selectivity ratio is close to unity. The selectivity ratio is found to increase with increase in the value of K_1 for independent and parallel reactions, while the effect is reversed for series reactions. When the value of K_2 is less than unity, the selectivity ratio is always greater than unity for independent reactions and the value increases

with decrease in K_2 or increase in ϕ_M. For such reactions when the value of K_2 is greater than unity, S_R decreases rapidly with increase in the value of K_2. For parallel and series reactions selectivity ratio decreases monotonically as the value of K_2 is decreased. When $K_A p_o$ is varied, the change in selectivity ratio is insignificant, if presented as a function of ϕ_M. However, when S_R values are plotted as a function of ordinary Thiele parameter, it increases with increase in the $K_A p_o$ value. The effect of increase in the value of diffusivity ratio, D_B/D_A, is significant for all the reactions and the value of S_R increases with increase in D_B/D_A. Increase in diffusivity of component C increases selectivity ratio for independent and parallel reactions but for series reactions, S_R is found to decrease. The effect of changing the diffusivity ratio D_D/D_A is insignificant for all the reactions. For independent reactions, the effect of change in the diffusivity ratio of two reactants, D_E/D_A, is similar to that of K_2.

The effect of change in the value of adsorption equilibrium constant ratios K_B/K_A, K_C/K_A, K_D/K_A and K_E/K_A on selectivity ratio is relatively insignificant. For independent and series reactions, selectivity ratio is found to increase, while for parallel reactions it decreases with increase in the value of K_B/K_A, K_C/K_A and K_D/K_A. Comparatively, changes in K_C/K_A has maximum effect on selectivity ratio. For independent reactions, the selectivity ratio is found to increase with increase in the value of K_E/K_A for ϕ_M values upto two, but for values of ϕ_M larger than 2.3, S_R decreases with increase in the value of K_E/K_A.

CHAPTER - I

INTRODUCTION

A. Background

When the reaction takes place in a porous catalyst mass, the fluid reactant has to diffuse inside the catalyst particle to make the effective use of the surface area available in its pores since most of the surface area is inside the pores as pore-walls. The reactants are chemisorbed and then react to form the chemisorbed product. The product molecules are then desorbed and diffuse out of the catalyst particle to the surface from which it is transferred to the bulk of the fluid. Each of these steps offer some resistance and the rate of reaction taking place in a catalyst pore depends upon the magnitude of these resistances. In the past, expressions for the rate of reaction in a catalyst pore are obtained taking into account these resistances. If all these resistances are considered together, the rate expression becomes too involved and in many cases it is not possible to obtain the rate expression in terms of measurable quantities. For this reason generally it is assumed that out of all these steps, one of them offer maximum resistance and accordingly all other resistances are neglected. Thus the rate of reaction equals the rate of the slowest step.

As a result of pore diffusion there exists a concentration gradient inside the pore and hence the reaction takes

place with different rates at different positions in the
catalyst pore. This effects the activity of the catalyst
which is measured in terms of effectiveness factor which is
defined as the actual rate of reaction in the pore divided
by the rate of reaction if there is no concentration gradient
due to pore diffusion. In complex reactions where more than
one reaction is taking place, quite often, different reactions
are effected in a different way and there is a change in
selectivity. The term selectivity is generally defined as
the rate of the desired reaction divided by the rate of
disappearance of the key reactant.

B. Literature Review

The effect of diffusion in a catalyst pore was first
treated by Damkohler [1], Thiele [2] and Zeldowitch [3]. All
of them considered first order irreversible reaction and
assumed that the Fick's law of diffusion holds good. A new
term, Thiele parameter $\emptyset$, was introduced which is qualitativel;
the measure of the effect of pore diffusion on chemical
reaction. The effectiveness factor was calculated as a
function of Thiele parameter and it is observed that at
higher values of Thiele parameter the effect is more while
at values less than 0.5 the effect is negligible. Later the
analysis was extended to include a wide range of reaction

order, pellet geometries and changes in number of molecules by Wheeler [4] and Weiz and Prater [5].

In catalytic reactions, the rate expressions are not simple first or second order. To account for the effect of adsorption, Langmuir-Hinshelwood type of rate expressions are to be used. For the first time Chu and Hougen [6] considered the effect of adsorption on effectiveness factor. They analyzed first order irreversible reaction A $\longrightarrow$ B where the product adsorption is neglected. Roberts and Satterfield [7. 8] analyzed the reaction, A + bB $\longrightarrow$ Products, assuming first and second order irreversible reaction kinetics. Schneider and Mitschka [9, 10, 11 and 12] and Kao and Satterfield [13] considered first order reversible reaction, A $\rightleftharpoons$ B, and showed that the retardation effect (due to pore diffusion) is more for reversible reaction than for irreversible reaction.

For complex reactions the effect of pore diffusion on selectivity was studied by Wheeler [14] who designated three fundamentally different types of selectivity, since each is effected quite differently by the pore diffusion. Selectivity for independent reactions has been studied by Wheeler [14] for parallel reaction by Ostergaard [15] and Powlowski [16] and for series reactions by Carberry [17]

Weiz [5] and Wheeler [14]. All of them have considered simple first or higher order reactions with simple rate expression. Recently Dwyer [18] has studied selectivity effect by the competition among the three rate processes' that is, desorption, diffusion and surface reaction, in deuterium exchange of neopentane.

C. Thesis Objectves

In the present work, effect of pore diffusion on selectivity of complex reactions is studied using Langmuir - Hinshelwood type of rate expressions which takes into account the effect of adsorption on the rate of reaction. Since there can be a wide variety of reactions, the following are considered for detailed study:

    1. Independent Reactions:

        $A \rightleftharpoons B + C$

        $E \longrightarrow D + C$
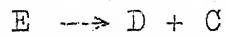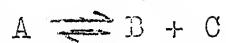
    2. Parallel Reactions:

        $2A \rightleftharpoons B + C$

        $A \longrightarrow D + C$
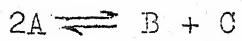
    3. Series Reactions:

        $A \rightleftharpoons B + C$

        $B \longrightarrow D + C$
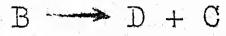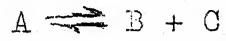
To consider the effect of reversibility, first of the two reactions in each case is taken as reversible. For independ

and series reactions, single site mechanism is considered
for both the reactions where B and D react in the adsorbed
state while C reacts in the fluid phase. For parallel
reactions, first reaction is considered as reversible second
order with dual site mechanism while for second reaction,
single site mechanism is considered where D is reacting in the
adsorbed state and C in the fluid phase. For all these
reactions, rate expressions are considered where the surface
reaction is controlling and reaction is considered in an
infinite slab with cylindrical pores. Selectivity thus
obtained is compared with the selectivity calculated in the
absence of diffusion effects and the ratio of two selecti-
vities, with and without diffusion, is presented as a
function of Thiele parameter for various reaction parameters.

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CHAPTER - II

MATHEMATICAL FORMULATION OF THE PROBLEM

A. Independent Reactions

When two reactions with different reactants are
taking place on a catalyst, the reactions are called in-
dependent reactions. Examples of this kind of reactions
are hydrogenation of a mixture of aromatic and olefinic
compounds, dehydrogenation of a mixture of napththenic
and paraffinic compounds and cracking of a mixture of hydro-
carbons. The following reaction scheme is considered for
detailed study.

$$A \; \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \; B + C \tag{1}$$

$$E \; \overset{k_2}{\longrightarrow} \; D + C$$
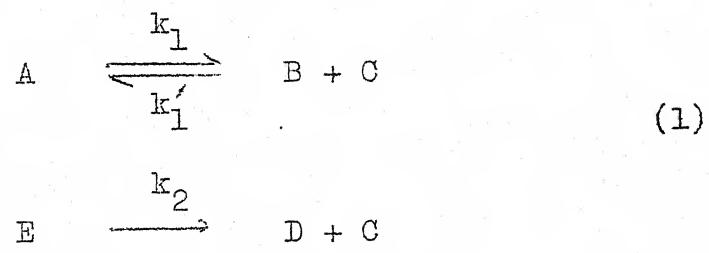
If single site mechanism is assumed for both the reactions,
where component C is reacting in the gas phase and surface
reaction controls the rate of reaction, the following rate
expressions can be obtained for the components A and E.

$$-r_A = \frac{k_1 \, K_A (p_A - \dfrac{p_B p_C}{K})}{(1 + \sum\limits_i K_i p_i)} \tag{2a}$$

$$-r_E = \frac{k_2\, K_E\, p_E}{(1 + \sum_i K_i p_i)} \qquad (2b)$$

Where r_A and r_E are the rate of formation of component A and E per unit pore volume k_1, k_1' and k_2 are the reaction rate constants for the adsorbed species in the direction indicated in equation 1, K_i is the adsorption equilibrium constant for component i, p_i is the partial pressure of component i, K is the equilibrium constant for the first reaction and subscript i stands for all the components present in the reaction mixture viz., A, B, C, D and E. The rate of reaction of other components can be obtained from simple stoichiometry.

$$r_B = -r_A \qquad (3a)$$

$$r_D = -r_E \qquad (3b)$$

$$r_C = r_B + r_D \qquad (3c)$$

Diffusion inside the pore:

At steady state, a mass balance of the component diffusing in and out from a small thin shell of thickness dz at a distance z from the pore-mouth becomes
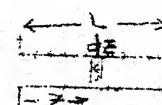
(Rate of diffusion in the direction of z at z = z) - (Rate of diffusion in the direction of z at z = z + dz) = Rate of reaction in the shell.

$$-S \cdot D_A \left(\frac{dC_A}{dz} \right) - \left[-SD_A \left(\frac{dC_A}{dz} + \frac{d^2C_A}{dz^2} dz \right) \right] = - Sdz \; r_A \qquad (4)$$

$$\text{or} \; D_A \; \frac{d^2C_A}{dz^2} = - \; r_A \qquad (5a)$$

Where S is the cross-sectional area of the pore, C_A is the concentration of component A and D_A is the diffusivity of component A.

The above equation is valid if transport of material is only due to diffusion and bulk transport due to pressure gradient is neglected. However, whenever there is change in number of moles, pressure gradient will exist within the pore. Otani et. al.[19] have studied the effect of pressure gradients on the effectiveness of porous catalysts and observed that for small capillaries where Knudsen diffusion predominates the influence is insignificant. For a typical bidisperse catalyst pellet, they concluded that the effect can be important only if the change in moles exceeds two.

In general,

$$D_i \; \frac{d^2C_i}{dz^2} = - \; r_i \qquad (5b)$$

Substitution of the values of r_A and r_B from equation (5) in equation (3)a gives

$$D_B \frac{d^2C_B}{dz^2} = - D_A \frac{d^2C_A}{dz^2}$$

Integrating twice and substituting the boundary conditions

$$C_i(\text{at } z = o) = C_{io}$$

and

$$\frac{dC_i}{dz} (\text{at } z = 1) = 0$$

with L as the length of the pore, the following equation is obtained

$$C_B = C_{Bo} + \frac{D_A}{D_B}(C_{Ao} - C_A) \qquad (6)$$

Equation 6 is valid when diffusion constants are independent of the position within the pore, that is z and concentration. This condition is satisfied only for small pores where Knudsen diffusion is predominant. If we assume ideal gas behaviour, then $C = P/RT$ and

$$p_B = p_{Bo} + \frac{D_A}{D_B}(p_{Ao} - p_A) \qquad (7a)$$

Similarly, $p_D = p_{Do} + \frac{D_E}{D_D}(p_{Eo} - p_E) \qquad (7b)$

and

$$p_C = p_{Co} + \frac{D_A}{D_C}(p_{Ao} - p_A) + \frac{D_E}{D_C}(p_{Eo} - p_E) \qquad (7c)$$

These values of partial pressure when substituted in equation 2a and eliminating r_A from equation 5a the following equation is obtained

$$k_1 K_A \left[p_A - \frac{1}{K} \left[p_{Do} + \frac{D_A}{D_B}(p_{Ao} - p_A) \right] \right] \left[p_{Co} + \frac{D_A}{D_C}(p_{Ao} - p_A) + \right.$$

$$\frac{D_A}{RT} \frac{d^2 p_A}{dz^2} = \frac{\frac{D_E}{D_C}(p_{Eo} - p_E) \Big] \Big]}{\left\{ 1 + K_A p_A + K_B \left[p_{Bo} + \frac{D_A}{D_B}(p_{Ao} - p_A) \right] + K_C \left[p_{Co} + \frac{D_A}{D_C}(p_{Ao} - p_A) + \right.}$$ (8a)

$$\frac{D_E}{D_C}(p_{Eo} - p_E) \Big] + K_D \left[p_{Do} + \frac{D_E}{D_D}(p_{Eo} - p_E) \right] + K_E p_E \Big\}$$

Similarly,

$$\frac{D_E}{RT} \frac{d^2 p_E}{dz^2} = \frac{k_2 K_E p_E}{\left\{ 1 + K_A p_A + K_B \left[p_{Bo} + \frac{D_A}{D_B}(p_{Ao} - p_A) \right] + K_C \left[p_{Co} + \frac{D_A}{D_C}(p_{Ao} - p_A) + \right.}$$ (8b)

$$\frac{D_E}{D_C}(p_{Eo} - p_E) \Big] + K_D \left[p_{Do} + \frac{D_E}{D_D}(p_{Eo} - p_E) \right] + K_E p_E \Big\}$$

Defining the following dimensionless parameters

$\varphi = p/p_o$, $\eta = z/L$, and $K_1 = K/p_o$ (where p_o is the pressure at the pore mouth) the equation 8 becomes

$$\frac{d^2 \varphi_A}{d\eta^2} = \frac{\phi^2 \left[\varphi_A - (\alpha - \frac{D_A}{D_B} \varphi_A)(\beta - \frac{D_A}{D_C} \varphi_A - \frac{D_E}{D_C} \varphi_E)/K_1 \right]}{(\omega' + \gamma' \varphi_A + \delta' \varphi_E)}$$ (9a)

$$\frac{d^2 \varphi_E}{d\eta^2} = \phi^2 \frac{1}{K_2} \frac{D_A}{D_E} \frac{\varphi_E}{(\omega' + \gamma' \varphi_A + \delta' \varphi_E)}$$ (9b)

Where

$$\phi = L \sqrt{\frac{k_1 K_A RT}{D_A}}$$ (10a)

$$\alpha = \varphi_{Bo} + \frac{D_A}{D_B} \varphi_{Ao} \tag{10b}$$

$$\beta = \varphi_{Co} + \frac{D_A}{D_C} \varphi_{Ao} + \frac{D_E}{D_C} \varphi_{Eo} \tag{10c}$$

$$\omega' = 1 + K_A p_o [\alpha \frac{K_B}{K_A} + \beta \frac{K_C}{K_A} + \frac{K_D}{K_A} (\varphi_{Do} + \frac{D_E}{D_D} \varphi_{Eo})] \tag{10d}$$

$$\gamma' = K_A p_o (1 - \frac{K_B}{K_A} \frac{D_A}{D_B} - \frac{K_C}{K_A} \frac{D_A}{D_C}) \tag{10e}$$

$$\delta' = K_A p_o (\frac{K_E}{K_A} - \frac{K_C}{K_A} \frac{D_E}{D_C} - \frac{K_D}{K_A} \frac{D_E}{D_D}) \tag{10f}$$

$$K_1 = \frac{k_1 K_A}{k_1' K_B p_o} \tag{10g}$$

$$K_2 = \frac{k_1 K_A}{k_2 K_E} \tag{10'}$$

The numerator and denominator in equations 9a and 9b when divided by $1 + K_A p_o$, we get

$$\frac{d^2 \varphi_A}{d\eta^2} = \frac{\emptyset_M^2 [\varphi_A - (\alpha - \frac{D_A}{D_B} \varphi_A)(\beta - \frac{D_A}{D_C} \varphi_A - \frac{D_E}{D_C} \varphi_E)/K_1]}{(\omega + \gamma \varphi_A + \delta \varphi_E)} \tag{11a}$$

$$\frac{d^2 \varphi_E}{d\eta^2} = \emptyset_M^2 \frac{1}{K_2} \frac{D_A}{D_E} \frac{\varphi_E}{(\omega + \gamma \varphi_A + \delta \varphi_E)} \tag{11b}$$

Where $\emptyset_M = L\sqrt{\frac{k_1 K_A RT}{D_A (1 + K_A p_o)}}$ \tag{12a}

$$\omega = \frac{1}{1+K_A p_o} + \frac{K_A p_o}{1+K_A p_o}[\alpha \frac{K_B}{K_A} + \beta \frac{K_C}{K_A} + \frac{K_D}{K_A}(\varphi_{Do} + \frac{D_E}{D_D}\varphi_{Eo})] \tag{12b}$$

$$\gamma = \frac{K_A p_o}{1+K_A p_o} (1 - \frac{K_B}{K_A}\frac{D_A}{D_B} - \frac{K_C}{K_A}\frac{D_A}{D_C}) \tag{12c}$$

$$\delta = \frac{K_A p_o}{1+K_A p_o} (\frac{K_E}{K_A} - \frac{K_C}{K_A}\frac{D_E}{D_C} - \frac{K_D}{K_A}\frac{D_E}{D_D}) \tag{12d}$$

with other constants remaining unchanged.

Equations 11a and 11b are to be solved with the following boundary conditions

$$\varphi_A(\text{at } \eta = 0) = \varphi_{Ao}$$
$$\varphi_E(\text{at } \eta = 0) = \varphi_{Eo} \tag{13}$$
$$\frac{d\varphi_A}{d\eta} (\text{at } \eta = 1) = \frac{d\varphi_E}{d\eta} (\text{at } \eta = 1) = 0$$

The last boundary condition is obtained because no reaction and hence no diffusion can take place at the end of the pore. Recognizing that the overall reaction rate within the pore equals the rate of mass transfer across the pore mouth, the rates of reactions of A and E will respectively be proportional to $D_A \frac{d\varphi_A}{d\eta}\Big|_{\eta=0}$ and $D_E \frac{d\varphi_E}{d\eta}\Big|_{\eta=0}$ and, therefore selectivity with diffusion effects

$$S_D = \frac{\text{rate of reaction of A within the pore}}{\text{rate of reaction of E within the pore}}$$

$$= \frac{D_A}{D_E} \frac{\frac{d\varphi_A}{d\eta}\Big|_{\eta=0}}{\frac{d\varphi_E}{d\eta}\Big|_{\eta=0}} \tag{14}$$

The rate of reaction without diffusion effect can be expressed as

$$r_A = \frac{k_1 K_A p_0 \left(\varphi_{Ao} - \frac{\varphi_{Bo} \varphi_{Co}}{K_1} \right)}{(1 + p_0 \sum_i K_i \varphi_{io})} \tag{15a}$$

$$r_E = \frac{k_2 K_E p_0 \varphi_{Eo}}{(1 + p_0 \sum_i K_i \varphi_{io})} \tag{15b}$$

and selectivity without diffusion

$$S_o = \frac{r_A}{r_E} = \frac{k_1 K_A \left(\varphi_{Ao} - \frac{\varphi_{Bo} \varphi_{Co}}{K_1} \right)}{k_2 K_E \varphi_{Eo}} \tag{16}$$

and selectivity ratio S_R is defined as

$$S_R = S_D / S_o$$

Special Case:

Initially when no products are present, and also the two reactants are present in equal proportion, then

$$\varphi_{Bo} = \varphi_{Co} = \varphi_{Do} = 0 \tag{17a}$$

$$\varphi_{Ao} = \varphi_{Eo} = 0.5 \tag{17b}$$

$$\alpha = 0.5 \frac{D_A}{D_B} \tag{17c}$$

$$\beta = 0.5 \left(\frac{D_A}{D_C} + \frac{D_E}{D_C} \right) \tag{17d}$$

$$\omega = \frac{1}{1+K_A p_o} + \frac{K_A p_o}{1+K_A p_o} \left[.5 \frac{D_A}{D_B} \frac{K_B}{K_A} + .5 \left(\frac{D_A}{D_C} + \frac{D_E}{D_C}\right) \frac{K_C}{K_A} + .5 \frac{D_E}{D_D} \frac{K_D}{K_A} \right] \quad (17e)$$

and $\quad S_O = \frac{k_1}{k_2} \frac{K_A}{K_E} = K_2 \quad$ (17f)

Therefore $S_R = \frac{1}{K_2} \frac{D_A}{D_E} \frac{\frac{d\varphi_A}{d\eta} \eta=0}{\frac{d\varphi_E}{d\eta} \eta=0}$ (17g)

with other terms unchanged.

To get selectivity ratio, the values of $\frac{d\varphi_A}{d\eta} \eta=0$ and $\frac{d\varphi_E}{d\eta} \eta=0$ are to be obtained. These are actually the missing initial conditions of the nonlinear simultaneous differential equations (equations 11a and 11b) with boundary conditions given by equation 13.

B. Parallel Reactions

When two or more reactions with same reactants are taking place on a catalyst the reactions are called parallel reactions. Examples of this kind of reactions are dehydration of alcohols to olefins and ethers, decomposition of formic acid and catalytic cracking. The following reaction scheme is considered for detailed study.

$$2A \underset{k_1}{\overset{k_1}{\rightleftharpoons}} B + C$$

$$A \xrightarrow{k_2} D + C$$
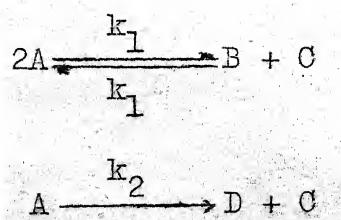
If dual site mechanism is assumed for the first
reaction and single site for the second reaction and also
if it is assumed that the surface reaction controls the rate
of reaction, the following rate expressions can be obtained
for the component B and D

$$r_B = \frac{k_1 K_A^2 (p_A^2 - \frac{p_B p_C}{K_1})}{(1 + \sum_i K_i p_i)^2} \tag{19a}$$

$$r_D = \frac{k_2 K_A p_A}{(1 + \sum_i K_i p_i)} \tag{19b}$$

Where r_B and r_D are the rate of formation of component B
and D per unit volume and subscript i stands for all the
components present in the reaction mixture. The rate of
reaction of other components can be obtained from simple
stoichiometry

$$-r_A = 2 r_B + r_D \tag{20a}$$

$$r_C = r_B + r_D \tag{20b}$$

Substituting equation 5 in equation 20 and integrating the
equations thus obtained and substituting the proper boundary
conditions, the following equations are obtained.

$$p_A = p_{Ao} - \frac{2D_B}{D_A}(p_B - p_{Bo}) - \frac{D_D}{D_A}(p_D - p_{Do}) \tag{21a}$$

$$p_C = p_{Co} + \frac{D_B}{D_C}(p_B - p_{Bo}) + \frac{D_D}{D_C}(p_D - p_{Do}) \tag{21b}$$

These values of partial pressure when substituted in equation 19a and eliminating r_A from equation 5b the following equation is obtained

$$k_1 K_A^2 \left[\left(p_{Ao} + \frac{2D_B}{D_A} p_{Bo} + \frac{D_D}{D_A} p_{Do} - \frac{2D_B}{D_A} p_B - \frac{D_D}{D_A} p_D \right)^2 - \right.$$

$$-\frac{D_B}{RT} \frac{d^2 p_B}{dz^2} = \frac{\frac{p_B}{K_1} \left(p_{Co} - \frac{D_B}{D_C} p_{Bo} - \frac{D_D}{D_C} p_{Do} + \frac{D_B}{D_C} p_B + \frac{D_D}{D_C} p_D \right) \right]}{\left\{ 1 + K_A \left[p_{Ao} - \frac{2D_B}{D_A} (p_B - p_{Bo}) - \frac{D_D}{D_A} (p_D - p_{Do}) \right] + K_B p_B + \right.} \qquad (22a)$$

$$\left. K_C \left[p_{Co} - \frac{D_B}{D_C} p_{Bo} - \frac{D_D}{D_C} p_{Do} + \frac{D_B}{D_C} p_B + \frac{D_D}{D_C} p_D \right] + K_D p_D \right\}^2$$

Similarly

$$-\frac{D_D}{RT} \frac{d^2 p_D}{dz^2} = \frac{k_2 K_A \left(p_{Ao} + \frac{2D_B}{D_A} p_{Bo} + \frac{D_D}{D_A} p_{Do} - \frac{2D_B}{D_A} p_B - \frac{D_D}{D_A} p_D \right)}{\left\{ 1 + K_A \left[p_{Ao} - \frac{2D_B}{D_A} (p_B - p_{Bo}) - \frac{D_D}{D_A} (p_D - p_{Do}) \right] + K_B p_B + \right.} \qquad (22b)$$

$$\left. K_C \left[p_{Co} - \frac{D_B}{D_C} p_{Bo} - \frac{D_D}{D_C} p_{Do} + \frac{D_B}{D_C} p_B + \frac{D_D}{D_C} p_D \right] + K_D p_D \right\}$$

Introducing dimensionless pressure and length φ and η respectively in equations 22 the following equations are obtained.

$$\frac{d^2 \varphi_B}{d\eta^2} = -\frac{\emptyset^2 \frac{D_A}{D_B} K_A p_0 \left[\left(\alpha_1 - \frac{2D_B}{D_A} \varphi_B - \frac{D_D}{D_A} \varphi_D \right)^2 - \frac{\varphi_B}{K_1} \left(\beta_1 + \frac{D_B}{D_C} \varphi_B + \frac{D_D}{D_C} \varphi_D \right) \right]}{\left(\omega_1' + \gamma_1' \varphi_B + \delta_1' \varphi_D \right)^2}$$

$$(23a)$$

$$\frac{d^2 \varphi_D}{d\eta^2} = \frac{\emptyset^2 \frac{1}{K_2} \frac{D_A}{D_D} \left(\alpha_1 - \frac{2D_B}{D_A} \varphi_B - \frac{D_D}{D_A} \varphi_D \right)}{\left(\omega_1' + \gamma_1' \varphi_B + \delta_1' \varphi_D \right)} \qquad (23b)$$

where

$$\alpha_1 = \varphi_{Ao} + \frac{2D_B}{D_A}\varphi_{Bo} + \frac{D_D}{D_A}\varphi_{Do} \qquad (24a)$$

$$\beta_1 = \varphi_{Co} - \frac{D_B}{D_C}\varphi_{Bo} - \frac{D_D}{D_C}\varphi_{Do} \qquad (24b)$$

$$\omega_1 = 1 + K_A p_o(\alpha_1 + \frac{K_C}{K_A}\beta_1) \qquad (24c)$$

$$\gamma_1 = K_A p_o\left(\frac{K_B}{K_A} - \frac{2D_B}{D_A} + \frac{K_C}{K_A}\frac{D_B}{D_C}\right) \qquad (24d)$$

$$\delta_1 = K_A p_o\left(\frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{K_C}{K_A}\frac{D_D}{D_C}\right) \qquad (24e)$$

$$K_1 = k_1 K_A^2 / k_1 K_B K_C \qquad (24f)$$

$$K_2 = k_1/k_2 \qquad (24g)$$

Taking out $(1+K_A p_o)^2$ and $(1+K_A p_o)$ from the denominator of equations 23a and 23b respectively, the following equations are obtained.

$$\frac{d^2\varphi_B}{d\eta^2} = -\frac{\phi_M^2\left(\frac{D_A}{D_B}\right)\frac{K_A p_o}{1+K_A p_o}\left[\left(\alpha_1 - 2\frac{D_B}{D_A}\varphi_B - \frac{D_D}{D_A}\varphi_D\right)^2 - \frac{\varphi_B}{K_1}\left(\beta_1 + \frac{D_B}{D_C}\varphi_B + \frac{D_D}{D_C}\varphi_D\right)\right]}{\left(\omega_1 + \gamma_1\varphi_B + \delta_1\varphi_D\right)^2} \qquad (25a)$$

$$\frac{d^2\varphi_D}{d\eta^2} = -\frac{\phi_M^2\frac{1}{K_2}\frac{D_A}{D_D}\left(\alpha_1 - \frac{2D_B}{D_A}\varphi_B - \frac{D_D}{D_A}\varphi_D\right)}{\left(\omega_1 + \gamma_1\varphi_B + \delta_1\varphi_D\right)} \qquad (25b)$$

where

$$\omega_1 = \frac{1}{1+K_A p_o} + \frac{K_A p_o}{1+K_A p_o}\left(\alpha_1 + \frac{K_C}{K_A}\beta_1\right) \qquad (26a)$$

$$\gamma_1 = \frac{K_A p_o}{1+K_A p_o}\left(\frac{K_B}{K_A} - \frac{2D_B}{D_A} + \frac{K_C}{K_A}\frac{D_B}{D_C}\right) \qquad (26b)$$

$$\delta_1 = \frac{K_A p_o}{1+K_A p_o}\left(\frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{K_C}{K_A}\frac{D_D}{D_C}\right) \qquad (26c)$$

with other constants remaining unchanged.

Equations 23a and 23b are to be solved with the following boundary conditions

$$\varphi_B(\eta = 0) = \varphi_{Bo} \tag{27a}$$

$$\varphi_D(\eta = 0) = \varphi_{Do} \tag{27b}$$

$$\frac{d\varphi_B}{d\eta}(\eta = 1) = \frac{d\varphi_D}{d\eta}(\eta = 1) = 0 \tag{27c}$$

The rate of formation of B and D will be proportional to $D_B \frac{d\varphi_B}{d\eta}\Big|_{\eta=0}$ and $D_D \frac{d\varphi_D}{d\eta}\Big|_{\eta=0}$ respectively, and therefore,

selectivity with diffusion effects.

$$S_D = \frac{\text{Rate of formation of B within the pore}}{\text{Rate of disappearance of A within the pore}}$$

$$= \frac{\dfrac{D_B}{D_A}\dfrac{d\varphi_B}{d\eta}\Big|_{\eta=0}}{2\dfrac{D_B}{D_A}\dfrac{d\varphi_B}{d\eta}\Big|_{\eta=0} + \dfrac{D_D}{D_A}\dfrac{d\varphi_D}{d\eta}\Big|_{\eta=0}} \tag{28}$$

The rate of reaction without diffusion effects can be expressed as

$$r_B = \frac{k_1 K_A^2 p_o^2 (\varphi_{Ao}^2 - \varphi_{Bo}\varphi_{Co}/K_1)}{(1 + p_o \sum_i K_i \varphi_{io})^2} \tag{29a}$$

$$r_D = \frac{k_2 K_A p_o \varphi_{Ao}}{(1 + p_o \sum_i K_i \varphi_{io})} \tag{29b}$$

and selectivity without diffusion

$$S_O = \frac{r_B}{2r_B + r_D} = \frac{r_B / r_D}{2r_B / r_D + 1}$$

$$= \frac{K_2 K_A p_o (\varphi_{Ao} - \frac{\varphi_{Bo} \varphi_{Co}}{\varphi_{Ao} K_1})/(1 + p_o \sum_i K_i \varphi_{io})}{[1 + 2K_2 K_A p_o (\varphi_{Ao} - \frac{\varphi_{Bo}}{\varphi_{Ao}} \frac{\varphi_{Co}}{K_1})/(1 + p_o \sum_i K_i \varphi_{io})]} \tag{30}$$

and selectivity ratio will be

$$S_R = \frac{S_D}{S_o}$$

Special Case:

Initially when no products are present

$$\varphi_{Bo} = \varphi_{Co} = \varphi_{Do} = 0 \tag{31a}$$

$$\varphi_{Ao} = 1 \text{ (pure reactant)} \tag{31b}$$

$$\alpha_1 = 1 \tag{31c}$$

$$\beta_1 = 0 \tag{31d}$$

$$\omega_1 = 1 \tag{31e}$$

and $$S_o = \frac{K_2 K_A p_o}{1 + K_A p_o (1 + 2K_2)} \tag{31f}$$

Therefore $$S_R = \frac{1 + K_A p_o (1 + 2K_2)}{K_2 K_A p_o} \cdot \frac{\frac{D_D}{D_A} \frac{d\varphi_B}{d\eta}\Big|_{\eta=0}}{2\frac{D_B}{D_A} \frac{d\varphi_B}{d\eta}\Big|_{\eta=0} + \frac{D_D}{D_A} \frac{d\varphi_D}{d\eta}\Big|_{\eta=0}} \tag{31g}$$

with other terms unchanged.

To get selectivity ratio, the values of $\frac{d\varphi_B}{d\eta}\Big|_{\eta=0}$ and $\frac{d\varphi_D}{d\eta}\Big|_{\eta=0}$ are to be obtained.

C. Series Reactions

When the product of a reaction further reacts to form a new product(s), the reactions are called series reactions. Examples of this kind of reactions are dehydration of butanedial to form butadiene, and dehydrogenation of cyclohexane to cyclohexene and then to benzene. The following reaction scheme is considered for detailed study.

$$A \quad \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \quad B + C \qquad\qquad (32)$$

$$B \quad \overset{k_2}{\longrightarrow} \quad D + C$$
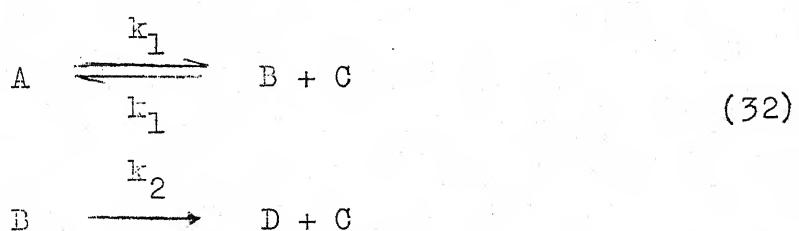
If single site mechanism is assumed for both the reactions, where C is reacting in the gas phase and surface reaction controls the rate of reaction, the following rate expressions can be obtained for the component B and D

$$r_B = \frac{k_1 K_A \left(p_A - \frac{p_B p_C}{K} - \frac{p_B}{K_2} \right)}{\left(1 + \sum_i K_i p_i \right)} \qquad (33a)$$

$$r_D = \frac{k_2 K_B p_B}{\left(1 + \sum_i K_i p_i \right)} \qquad (33b)$$

where K = equilibrium constant for the first reaction = $k_1 K_A / k_1' K_B$ and $K_2 = k_1 K_A / k_2 K_B$. The rate of reaction of

other components can be obtained from simple stoichiometry.

$$-r_A = r_B + r_D \tag{34a}$$

$$r_C = -r_A + r_D \tag{34b}$$

Substituting equation 5 in equation 34 and integrating the equations thus obtained and substituting the proper boundary conditions, the following equations are obtained

$$p_A = p_{Ao} - \frac{D_B}{D_A}(p_B - p_{Bo}) - \frac{D_D}{D_A}(p_D - p_{Do}) \tag{35a}$$

$$p_C = p_{Co} + \frac{D_B}{D_C}(p_B - p_{Bo}) + \frac{2D_D}{D_C}(p_D - p_{Do}) \tag{35b}$$

These values of partial pressure when substituted in equation 33a and eliminating r_B from equation 5b the following equation is obtained.

$$-\frac{D_B}{RT}\frac{d^2p_B}{dz^2} = \frac{k_1 K_A\left[p_{Ao} + \frac{D_B}{D_A}p_{Bo} + \frac{D_D}{D_A}p_{Do} - \frac{D_B}{D_A}p_B - \frac{D_D}{D_A}p_D - \frac{p_B}{K}\left(p_{Co} - \frac{D_B}{D_C}p_{Bo} - \frac{2D_D}{D_C}p_{Do} + \frac{D_B}{D_C}p_B + \frac{2D_D}{D_C}p_D\right) - \frac{p_B}{K_2}\right]}{\left[1 + K_A\left(p_{Ao} + \frac{D_B}{D_A}p_{Bo} + \frac{D_D}{D_A}p_{Do} - \frac{D_B}{D_A}p_B - \frac{D_D}{D_A}p_D\right) + K_B p_B + K_C\left(p_{Co} - \frac{D_B}{D_C}p_{Bo} - \frac{2D_D}{D_C}p_{Do} + \frac{D_B}{D_C}p_B + \frac{2D_D}{D_C}p_D\right) + K_D p_D\right]}$$

$$\tag{36a}$$

Similarly

$$-\frac{D_D}{RT}\frac{d^2 p_D}{dz^2} = \frac{k_2 K_B p_B}{[1+K_A(p_{Ao}+\frac{D_B}{D_A}p_{Bo}+\frac{D_D}{D_A}p_{Do}-\frac{D_B}{D_A}p_B-\frac{D_D}{D_A}\cdot p_D)+K_B p_B+}$$

$$K_C(p_{Co}-\frac{D_B}{D_C}p_{Bo}-\frac{2D_D}{D_C}p_{Do}+\frac{D_B}{D_C}p_B+\frac{2D_D}{D_C}p_D)+K_D p_D]$$

$$(36b)$$

Introducing dimensionless pressure and length φ and η respectively in equation 36, the following equations are obtained.

$$\frac{d^2 \varphi_B}{d\eta^2} = -\emptyset^2\frac{D_A}{D_B}\frac{[(\alpha_2-\frac{D_B}{D_A}\varphi_B-\frac{D_D}{D_A}\varphi_D)-\frac{p_B}{K_1}(\beta_2+\frac{D_B}{D_C}\varphi_B+\frac{2D_D}{D_C}\varphi_D)-\frac{\varphi_B}{K_2}]}{(\omega_2'+\gamma_2'\varphi_B+\delta_2'\varphi_D)} \quad (37a)$$

$$\frac{d^2 \varphi_D}{d\eta^2} = -\emptyset^2\frac{1}{K_2}\frac{D_A}{D_B}\frac{\varphi_B}{(\omega_2'+\gamma_2'\varphi_B+\delta_2'\varphi_D)} \quad (37b)$$

where

$$\alpha_2 = \varphi_{Ao}+\frac{D_B}{D_A}\varphi_{Bo}+\frac{D_D}{D_A}\varphi_{Do} \quad (38a)$$

$$\beta_2 = \varphi_{Co}-\frac{D_B}{D_C}\varphi_{Bo}-\frac{2D_D}{D_A}\varphi_{Do} \quad (38b)$$

$$\omega_2' = 1+K_A p_o(\alpha_2+\frac{K_C}{K_A}\beta_2) \quad (38c)$$

$$\gamma_2' = K_A p_o(\frac{K_B}{K_A}-\frac{D_B}{D_A}+\frac{K_C}{K_A}\frac{D_B}{D_C}) \quad (38d)$$

$$\delta_2' = K_A p_o(\frac{K_D}{K_A}-\frac{D_D}{D_A}+\frac{2K_C}{K_A}\frac{D_D}{D_C}) \quad (38e)$$

$$K_1 = \frac{k_1 K_A}{k_1' K_B p_o} \quad (38f)$$

Taking out $1+K_A p_o$ from the denominator of equation 37a and 37b and rearranging, the following equations are obtained.

$$\frac{d^2 \varphi_B}{d\eta^2} = - \varphi_M^2 \frac{D_A}{D_B} \frac{[\alpha_2 - (\frac{D_B}{D_A} + \frac{\beta}{K_1} + \frac{1}{K_2})\varphi_B - \frac{D_D}{D_A}\varphi_D - \frac{\varphi_B}{K_1}(\frac{D_B}{D_C}\varphi_B + \frac{2D_D}{D_C}\varphi_D)]}{(\omega_2 + \gamma_2 \varphi_B + \delta_2 \varphi_D)} \tag{39a}$$

$$\frac{d^2 \varphi_D}{d\eta^2} = - \varphi_M^2 \frac{1}{K_2} \frac{D_A}{D_D} \frac{\varphi_B}{(\omega_2 + \gamma_2 \varphi_B + \delta_2 \varphi_D)} \tag{39b}$$

where,

$$\omega_2 = \frac{1}{1+K_A p_o} + \frac{K_A p_o}{1+K_A p_o}(\alpha_2 + \frac{K_C}{K_A}\beta_2) \tag{40a}$$

$$\gamma_2 = \frac{K_A p_o}{1+K_A p_o}(\frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{2K_C}{K_A}\frac{D_B}{D_C}) \tag{40b}$$

$$\delta_2 = \frac{K_A p_o}{1+K_A p_o}(\frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{2K_C}{K_A}\frac{D_D}{D_C}) \tag{40c}$$

with other constants remaining unchanged.

Equations 39a and 39b are to be solved with the boundary conditions given by equation 27. The selectivity with diffusion effects is given by equation 28. The rate of reaction without diffusion effects can be expressed as

$$r_B = \frac{k_1 K_A p_o(\varphi_{Ao} - \frac{\varphi_{Bo}\varphi_{Co}}{K_1} - \frac{\varphi_{Bo}}{K_2})}{(1 + p_o \sum_i K_i \varphi_{io})} \tag{41a}$$

$$-r_A = r_B + r_D = \frac{k_1 K_A p_o(\varphi_{Ao} - \frac{\varphi_{Bo}\varphi_{Co}}{K_1})}{(1 + p_o \sum_i K_i \varphi_{io})} \tag{41b}$$

and selectivity without diffusion

$$S_0 = \frac{r_B}{r_B + r_D} = \frac{(\varphi_{Ao} - \varphi_{Bo}\varphi_{Co}/K_1 - \varphi_{Bo}/K_2)}{(\varphi_{Ao} - \varphi_{Bo}\varphi_{Co}/K_1)} \qquad (42)$$

and selectivity ratio will be

$$S_R = \frac{S_D}{S_0}$$

Special Case:

Initially when no products are present

$$\varphi_{Bo} = \varphi_{Co} = \varphi_{Do} = 0 \qquad (43a)$$

$$\varphi_{Ao} = 1 \text{ (pure reactant)} \qquad (43b)$$

$$\alpha_2 = 1 \qquad (43c)$$

$$\beta_2 = 0 \qquad (43d)$$

$$\omega_2 = 1 \qquad (43e)$$

and $\quad S_0 = 1 \qquad (43f)$

Therefore $S_R = \dfrac{\dfrac{D_B}{D_A} \dfrac{d\varphi_B}{d\eta}\Big|_{\eta=0}}{\dfrac{D_B}{D_A} \dfrac{d\varphi_B}{d\eta}\Big|_{\eta=0} + \dfrac{D_D}{D_A} \dfrac{d\varphi_D}{d\eta}\Big|_{\eta=0}} \qquad (43g)$

with other terms unchanged

To get selectivity ratio, the value of $\dfrac{d\varphi_B}{d\eta}\Big|_{\eta=0}$ and

$\dfrac{d\varphi_D}{d\eta}\Big|_{\eta=0}$ are to be obtained.

. . . .

CHAPTER - III

SOLUTION OF A SYSTEM OF NON-LINEAR BOUNDARY VALUE PROBLEMS

A. Introduction

In a nonlinear differential equation when some conditions are given at one point while the remaining conditions at some other point, the equations are called the nonlinear boundary value problem. These problems are much more difficult to handle both theoretically and computationally, and there is no general proof of the existance and the uniqueness of the solution to problems of this type. If all the conditions are known at one point, Runge-Kutta or predictor-corrector method [20] can be used to solve a system of non-linear equations. Accordingly, one method of solving non-linear boundary value problem will be to assume the missing initial conditions and solve these equations by one of the above mentioned methods. The final values are compared with the given boundary conditions,and the difference between the computed value and the true value is used to predict the missing initial conditions. Many a times, the solution of these equations is very sensitive to the guessed initial conditions and hence these guessed values must almost be

same as the true value. This difficulty becomes more severe, if the equations are of higher order or a large system of first order equations are to be solved.

Several techniques have since been developed to solve linear boundary value problems of first or higher order. These are discussed by Fox [21] and Keller [22]. One of the methods is to convert these equations into a set of difference equations and solve them algebraically. Bellman applied Newton-Raphsons method to convert non linear equations into linear equations which can then be solved by the method of superposition or by finite difference method. The technique of converting nonlinear equations into linear equations is named as quasilinearization and is discussed in his book [23]. Quasilinearization technique has also been applied to the solution of a number of chemical engineering problems by Lee [24, 25, 26].

Quasilinearization technique has been applied to solve the nonlinear differential equations obtained in the previous chapter for Thiele parameter greater than 2 and is discussed briefly in the next section. For values of Thiele parameter upto 2, a newer method based on the principle of invariant imbedding is developed and is discussed in the next chapter. This method is much faster than the method based on quasi-linearization.

B. Quasilinearization

Consider a system of two second order differential equations

$$\frac{d^2x}{dt^2} = f(x,y) = F \tag{1a}$$

$$\frac{d^2y}{dt^2} = g(x,y) = G \tag{1b}$$

with boundary conditions

$$x(0) = x_0 \tag{2a}$$

$$y(0) = y_0 \tag{2b}$$

$$\frac{dx}{dt}(1) = \frac{dy}{dt}(1) = 0 \tag{2c}$$

If the value of the function at nth iteration is known, the value at n+1th iteration can be found by the recurrence relation

$$\frac{d^2x_{n+1}}{dt^2} = f(x_n, y_n) + (x_{n+1} - x_n)\frac{\partial F}{\partial x_n} + (y_{n+1} - y_n)\frac{\partial F}{\partial y_n} \tag{3a}$$

$$\frac{d^2y_{n+1}}{dt^2} = g(x_n, y_n) + (x_{n+1} - x_n)\frac{\partial G}{\partial x_n} + (y_{n+1} - y_n)\frac{\partial G}{\partial y_n} \tag{3b}$$

These equations are linear and can be solved by the method of finite difference as discussed in the next section.

C. Finite Difference Method

The left hand side of equation 3 can be written as

$$\frac{d^2 x_{n+1}(t_k)}{dt^2} = \frac{1}{(\Delta t)^2}[x_{n+1}(t_{k+1}) - 2x_{n+1}(t_k) + x_{n+1}(t_{k-1})]$$
(4a)

$$\frac{d^2 y_{n+1}(t_k)}{dt^2} = \frac{1}{(\Delta t)^2}[y_{n+1}(t_{k+1}) - 2y_{n+1}(t_k) + y_{n+1}(t_{k-1})]$$
(4b)

To make the algebraic equation simpler y_{n+1} is equated to y_n and x_{n+1} is equated to x_n in equations 3a and 3b respectively. Substituting equation 4 in equation 3 and writing Δ for Δt the following relations are obtained:

$$\frac{1}{\Delta^2}x_{n+1}(t_{k-1}) - (\frac{2}{\Delta^2} + \frac{\partial F}{\partial x})x_{n+1}(t_k) + \frac{1}{\Delta^2}x_{n+1}(t_{k+1}) = F_n - x_n(t_k)\frac{\partial F}{\partial x}$$
(5a)

$$\frac{1}{\Delta^2}y_{n+1}(t_{k-1}) - (\frac{2}{\Delta^2} + \frac{\partial G}{\partial x})y_{n+1}(t_k) + \frac{1}{\Delta^2}y_{n+1}(t_{k+1}) = G_n - y_n(t_k)\frac{\partial G}{\partial y}$$
(5b)

If these equations are expanded for values of k=1 to N-1, equation 5a can be written as

$$a_1 x_{n+1}(t_1) + \frac{1}{\Delta^2}x_{n+1}(t_2) = V_1 - \frac{1}{\Delta^2}x_{n+1}(t_0)$$

$$\frac{1}{\Delta^2}x_{n+1}(t_1) + a_2 x_{n+1}(t_2) + \frac{1}{\Delta^2}x_{n+1}(t_3) = V_2$$

$$\frac{1}{\Delta^2} x_{n+1}(t_2) + a_3 \; x_{n+1}(t_3) + \frac{1}{\Delta^2} x_{n+1}(t_4) = V_3$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

$$\frac{1}{\Delta^2} x_{n+1}(t_{N-2}) + a_{N-1} x_{n+1}(t_{N-1}) + \frac{1}{\Delta^2} x_{n+1}(t_N) = V_{n-1} \qquad (6)$$

For our problem the boundary conditions are

$$x_{n+1}(t_0) = x_0 \qquad (7a)$$

and $\quad x_{n+1}(t_{N-1}) = x_{n+1}(t_N) \qquad (7b)$

These values are substituted in the above equation to get

$$\bar{A} \; \bar{x}_{n+1} = \bar{V} \qquad (8)$$

where matrix $\bar{A} = \begin{bmatrix} a_1 & 1/\Delta^2 & & & \\ 1/\Delta^2 & a_2 & 1/\Delta^2 & & \\ & 1/\Delta^2 & a_3 & 1/\Delta^2 & \\ & & & \ddots & \\ & & & 1/\Delta^2 & a_{N-1} \end{bmatrix} \qquad (9)$

$$\bar{x}_{n+1} = \begin{bmatrix} x_{n+1}(t_1) \\ x_{n+1}(t_2) \\ \vdots \\ \vdots \\ x_{n+1}(t_{N-1}) \end{bmatrix} \qquad (10)$$

and $\quad \bar{V} = \begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ \vdots \\ V_{N-1} \end{bmatrix} \qquad (11)$

with $\quad a_k = -\left(\dfrac{2}{\Delta^2} + \dfrac{\partial F}{\partial x}\right)$, $k = 1$ to $N-2$ $\qquad$ (12)

$$a_{N-1} = -\left(\dfrac{2}{\Delta^2} + \dfrac{\partial F}{\partial x}\right) + \dfrac{1}{\Delta^2}$$

and $\quad V_1 = F_n - x_n(t_1)\,\dfrac{\partial F}{\partial x} - \dfrac{x_0}{\Delta^2}$ $\qquad$ (13)

$$V_k = F_n - x_n(t_k)\,\dfrac{\partial F}{\partial x} \quad , \quad k = 2 \text{ to } N-1$$

Similar expressions for equation 5b are

$$\overline{B}\,\overline{y}_{n+1} = \overline{W} \qquad (14)$$

where $\overline{B} = \begin{bmatrix} b_1 & 1/\Delta^2 & & & \\ 1/\Delta^2 & b_2 & 1/\Delta^2 & & \\ & 1/\Delta^2 & b_3 & 1/\Delta^2 & \\ & & \ddots & \ddots & \\ & & & 1/\Delta^2 & b_{N-1} \end{bmatrix}$ $\qquad$ (15)

$$\overline{y}_{n+1} = \begin{bmatrix} y_{n+1}(t_1) \\ y_{n+1}(t_2) \\ \vdots \\ y_{n+1}(t_{N-1}) \end{bmatrix} \qquad (16)$$

and $\quad \overline{W} = \begin{bmatrix} W_1 \\ W_2 \\ \vdots \\ W_{N-1} \end{bmatrix}$ $\qquad$ (17)

with $\quad b_k = - \left(\dfrac{2}{\Delta^2} + \dfrac{\partial G}{\partial y} \right) \quad , \; k = 1 \text{ to } N-2$

$\qquad b_{N-1} = - \left(\dfrac{2}{\Delta^2} + \dfrac{\partial G}{\partial y} \right) + \dfrac{1}{\Delta^2} \qquad\qquad (18)$

and $\quad W_1 = \quad G_n - y_n(t_1) \dfrac{\partial G}{\partial y} - \dfrac{y_0}{\Delta^2}$

$\qquad W_k = G_n - y_n(t_k) \dfrac{\partial G}{\partial y} \quad , \; k = 2 \text{ to } N-1 \qquad (19)$

The method of solution consists of choosing a reasonable initial approximation of the function $x(t)$ and $y(t)$; call them $x_0(t)$ and $y_0(t)$. The better values $x_1(t)$ and $y_1(t)$ are obtained by solving equations 8 and 14. The improved value $x_1(t)$ and $y_1(t)$ now becomes the initial approximation and the better values are obtained by again solving equations 8 and 14. This process is continued till the two iteration gives nearly same values for $x(t)$ and $y(t)$. Equations 8 and 14 can be solved easily by the Thomas method [27] for tri-diagonal matrices.

CHAPTER - IV

INVARIANT IMBEDDING

SOLUTION OF A SYSTEM OF NONLINEAR BOUNDARY VALUE

PROBLEMS

A. Introduction

The principle of invariant imbedding was first used
by Ambarzumian [28] and was later applied by Chandrasekhar[29]
in treating the problem in radiative transfer. Bellman,
Kalaba and Wing used them in the study of transport theory
[30, 31, 32]. A more detailed bibliography is given in a
recent book by Lee [33] on Quasilinearization and Invariant
Imbedding. Recently Srinivasan and Koteswara Rao applied
this principle to age dependent birth and death processes [34].
Bellman et.al. [35, 36] used this principle to solve nonlinear
boundary value problem. Koenig [37] and more recently Lee [38]
has demonstrated the usefulness of this approach for obtaining
the missing initial condition of a second order differential
equation. The method discussed by Lee uses linear inter-
polation of values and is applicable only for a set of two
first order equations. For a system of larger number of
equations, Lee has suggested a method in which a set of partial
differential equations are to be solved.

B. Thesis Objectives

In the present work a new method is developed to get the missing initial conditions of a system of nonlinear differential equations of the boundary value type. The method is direct and requires significantly less computation time.

C. Mathematical Formulation

Consider a system of nonlinear differential equations

$$\frac{dx_i}{dt} = f_i(x_1, x_2, \ldots, x_n, y_1, y_2, \ldots, y_n, t)$$

$$\frac{dy_i}{dt} = g_i(x_1, x_2, \ldots, x_n, y_1, y_2, \ldots, y_n, t)$$

$$i = 1, 2, \ldots, n \qquad (1)$$

with boundary conditions

$$x_i(0) = c_{io} \qquad (2)$$

$$y_i(t_f) = 0$$

with $0 \leqslant t \leqslant t_f$, t_f is the final value of t.

To illustrate the approach, consider a system of only four non-linear two point boundary value equations.

$$\frac{dx_1}{dt} = f_1(x_1, x_2, y_1, y_2, t)$$

$$\frac{dx_2}{dt} = f_2(x_1, x_2, y_1, y_2, t)$$

$$\frac{dy_1}{dt} = g_1(x_1, x_2, y_1, y_2, t)$$

$$\frac{dy_2}{dt} = g_2(x_1, x_2, y_1, y_2, t) \tag{3}$$

with boundary conditions

$$x_1(0) = c_0$$
$$x_2(0) = d_0 \tag{4}$$
$$y_1(t_f) = 0$$
$$y_2(t_f) = 0$$

with $\quad 0 \leqslant t \leqslant t_f$

For solving these equations, consider a more general boundary conditions

$$x_1(a) = c$$
$$x_2(a) = d \tag{5}$$
$$y_1(t_f) = 0$$
$$y_2(t_f) = 0$$

with $\quad a \leqslant t \leqslant t_f$

Here a is the starting value of the independent variable t which varies from 0 to t_f. If $x_1(t_f)$ and $x_2(t_f)$ are known then it is no longer a boundary value problem and it becomes an initial value problem where final conditions are given. The missing initial conditions $y_1(a)$ and $y_2(a)$ will be obtained by non iterative direct method using invariant imbedding concept. It is apparent that the missing conditions $y_1(a)$ and $y_2(a)$ for the system represented by

equations 3 and 5 are not only the function of a, the starting value of the independent variable t, but also the function of initial conditions c and d, thus

$$y_1(a) = r(c,d,a) = r[x_1(a), x_2(a), a]$$
$$y_2(a) = s(c,d,a) = s[x_1(a), x_2(a), a]$$

(6)

For a process starting at $a + \Delta$, the missing initial condition $y_1(a + \Delta)$ can be related to $y_1(a)$ by the use of Taylors series.

$$y_1(a + \Delta) = y_1(a) + y_1(a)\Delta + \text{higher order terms}$$

(7)

Where $y_1'(a) = (\dfrac{dy_1}{dt})_{t=a}$

The value of $y_1(a)$ can be obtained from equation 3

$$y_1(a) = g_1[x_1(a), x_2(a), y_1(a), y_2(a), a]$$
$$= g_1[c,d,r(c,d,a), s(c,d,a), a]$$

(8)

Substituting equations 6 and 8 in equation 7 and neglecting higher order terms, the following relation is obtained

$$y_1(a + \Delta) = r(c,d,a) + g_1[c,d,r(c,d,a), s(c,d,a),a]\Delta$$

(9a)

Similarly

$$y_2(a+ \Delta) = s(c,d,a) + g_2[c,d,r(c,d,a), s(c,d,a),a]\Delta$$

(9b)

$$x_1(a+ \Delta) = c + f_1[c,d,r(c,d,a), s(c,d,a),a]\Delta \quad (9c)$$
$$x_2(a+ \Delta) = d + f_2[c,d,r(c,d,a), s(c,d,a),a]\Delta \quad (9d)$$

The values of $y_1(a + \Delta)$ and $y_2(a + \Delta)$ can also be obtained from equation 6, thus

$$y_1(a + \Delta) = r\,[x_1(a + \Delta),\ x_2(a + \Delta), a + \Delta\,] \qquad (10)$$

$$y_2(a + \Delta) = s\,[x_1(a + \Delta),\ x_2(a + \Delta), a + \Delta\,]$$

Substituting equations 9c and 9d in equation 10.

$$y_1(a + \Delta) = r[c + f_1[c,d,r\,(c,d,a),\ s(c,d,a),a]\Delta,$$
$$d + f_2[c,d,r(c,d,a),\ s(c,d,a),a]\Delta,\ a+\Delta]$$

$$(11a)$$

$$y_2(a+\Delta) = s[c + f_1[c,d,r(c,d,a),\ s(c,d,a),a]\Delta,$$
$$d + f_2[\ c,d,r(c,d,a),s(c,d,a),a]\Delta,\ a+\Delta\,]$$

$$(11b)$$

The desired relationship can be obtained by equating equations 9a and 11a.

$$r(c,d,a) + g_1[c,d,r(c,d,a),s(c,d,a),a]\Delta =$$
$$r[c+f_1[c,d,r(c,d,a),s(c,d,a),a]\Delta,\ d+f_2[c,d,r(c,d,a),$$
$$s(c,d,a),a]\Delta,\ a+\Delta\,]$$

$$(12a)$$

Similarly by equating equations 9b and 11b

$$s(c,d,a) + g_2[c,d,r(c,d,a),s(c,d,a),a]\Delta =$$
$$s[c+f_1[c,d,r(c,d,a),s(c,d,a),a]\Delta,\ d+f_2[c,d,r(c,d,a),$$
$$s(c,d,a),a]\Delta,\ a+\Delta\,]$$

$$(12b)$$

Equations 12a and 12b are the required difference equations and can be solved directly to obtain the missing initial conditions $r(c,d,a)$ and $s(c,d,a)$.

D. Illustrative Example

Consider the following non-linear two point boundary value problem.

$$\frac{d^2 x_1}{dt^2} = -\frac{(1-x_1-x_2)}{1+\frac{1}{2}(x_1+x_2)}$$

$$\frac{d^2 x_2}{dt^2} = -\frac{(1-x_1-x_2)^2 - x_2^2}{[1+\frac{1}{2}(x_1+x_2)]^2}$$

(13)

with boundary conditions

$$x_1(0) = c_0$$

$$x_2(0) = d_0$$

$$\left[\frac{dx_1}{dt}\right]_{t=1} = 0$$

$$\left[\frac{dx_2}{dt}\right]_{t=1} = 0$$

(14)

The system of equations given above is obtained when we consider diffusion and reaction in a cylindrical pore for a parallel reaction following Langmuir-Hinshelwood kinetic model.

Replace $\frac{dx_1}{dt}$ by y_1 and $\frac{dx_2}{dt}$ by y_2 to obtain

$$\frac{dx_1}{dt} = y_1$$

$$\frac{dx_2}{dt} = y_2$$

$$\frac{dy_1}{dt} = -\frac{(1-x_1-x_2)}{1+\frac{1}{2}(x_1+x_2)} = G_1(x_1, x_2)$$

$$\frac{dy_2}{dt} = -\frac{(1-x_1-x_2)^2-x_2^2}{[1+\frac{1}{2}(x_1+x_2)]^2} = G_2\,(x_1,x_2) \tag{15}$$

With more general boundary conditions

$$x_1(a) = c$$
$$x_2(a) = d$$
$$y_1(1) = 0 \tag{16}$$
$$y_2(1) = 0$$

Comparing equation 15 with equation 3.

$$f_1(x_1,x_2,y_1,y_2,t) = y_1$$
$$f_2(x_1,x_2,y_1,y_2,t) = y_2$$
$$g_1(x_1,x_2,y_1,y_2,t) = G_1(x_1,x_2) \tag{17}$$
$$g_2(x_1,x_2,y_1,y_2,t) = G_2(x_1,x_2)$$

Substituting equation 17 in equations 12a and 12b, equation 18 is obtained.

$$r(c,d,a) + G_1(c,d)\Delta = r[c+r(c,d,a)\Delta, d+s(c,d,a)\Delta, a+\Delta]$$
$$s(c,d,a) + G_2(c,d)\Delta = s[c+r(c,d,a)\Delta, d+s(c,d,a)\Delta, a+\Delta] \tag{18}$$

If Δ is small, the following approximations can be made

$$r[c+r(c,d,a)\Delta, d+s(c,d,a)\Delta, a+\Delta] =$$
$$\qquad r[c+r(c,d,a+\Delta)\Delta, d+s(c,d,a+\Delta)\Delta, a+\Delta]$$

and $\tag{19}$

$$s[c+r(c,d,a)\Delta, d+s(c,d,a)\Delta, a+\Delta] =$$
$$\qquad s[c+r(c,d,a+\Delta)\Delta, d+s(c,d,a+\Delta)\Delta, a+\Delta]$$

and equation 18 can be written as

$$r(c,d,a) = -G_1(c,d)\Delta + r[c+r(c,d,a+\Delta)\Delta, \quad d+s(c,d,a+\Delta)\Delta, a+\Delta]$$

$$s(c,d,a) = -G_2(c,d)\Delta + s[c+r(c,d,a+\Delta)\Delta, \quad d+s(c,d,a+\Delta) \quad, a+\Delta]$$

$$(20)$$

With boundary conditions at $t = 1$

$$r(c,d,1) = y_1(1) = 0$$
$$s(c,d,1) = y_2(1) = 0 \qquad (21)$$

Divide the duration of t, $0 \leqslant t \leqslant 1$ in N parts with increment Δ so that $N\Delta = 1$.

To get $r(c,d,1-\Delta)$ and $s(c,d,1-\Delta)$, substitute $1-\Delta$ for a in equation 20 thus.

$$r(c,d,1-\Delta) = -G_1(c,d)\Delta \qquad (22)$$
$$s(c,d,1-\Delta) = -G_2(c,d)\Delta$$

Put $a = 1 - 2\Delta$ in equation 20 and substitute equation 22 to get.

$$r(c,d,1-2\Delta) = -G_1(c,d)\Delta + r[c-G_1(c,d)\Delta^2, d-G_2(c,d)\Delta^2, 1-\Delta]$$

$$s(c,d,1-2\Delta) = -G_2(c,d)\Delta + s[c-G_1(c,d)\Delta^2, d-G_2(c,d)\Delta^2, 1-\Delta]$$

$$(23)$$

Let $c_1 = c-G_1(c,d)\Delta^2$

$$d_1 = d-G_2(c,d)\Delta^2 \qquad (24)$$

and since (from equation 22 by replacing c and d with c_1 and d_1 respectively)

$$r(c_1,d_1,1-\Delta) = -G_1(c_1,d_1)\Delta \qquad (25)$$
$$s(c_1,d_1,1-\Delta) = -G_2(c_1,d_1)\Delta$$

equation 23 simplifies to

$$r(c,d,1-2\Delta) = -[G_1(c,d) + G_1(c_1,d_1)]\Delta$$
$$s(c,d,1-2\Delta) = -[G_2(c,d) + G_2(c_1,d_1)]\Delta \qquad (26)$$

Similarly when $a = 1-3\Delta$

$$r(c,d,1-3\Delta) = -G_1(c,d)\Delta + r[c+r(c,d,1-2\Delta)\Delta,$$
$$d+s(c,d,1-2\Delta)\Delta, 1-2\Delta]$$
$$s(c,d,1-3\Delta) = -G_2(c,d)\Delta + s[c+r(c,d,1-2\Delta)\Delta,$$
$$d+s(c,d,1-2\Delta)\Delta, 1-2\Delta] \qquad (27)$$

Substituting equation 26 for $r(c,d,1-2\Delta)$ and $s(c,d,1-2\Delta)$

and defining

$$c_2 = c-[G_1(c,d) + G_1(c_1,d_1)]\Delta^2$$
$$d_2 = d-[G_2(c,d) + G_2(c_1,d_1)]\Delta^2 \qquad (28)$$

we get

$$r(c,d,1-3\Delta) = -G_1(c,d)\Delta + r(c_2,d_2,1-2\Delta)$$
$$s(c,d,1-3\Delta) = -G_2(c,d)\Delta + s(c_2,d_2,1-2\Delta) \qquad (29)$$

The last terms of the above equations can be calculated from

equation 26 so that;

$$r(c_2,d_2,1-2\Delta) = -[G_1(c_2,d_2) + G_1(c_1,d_1)]\Delta$$
$$s(c_2,d_2,1-2\Delta) = -[G_2(c_2,d_2) + G_2(c_1,d_1)]\Delta \qquad (30)$$

Where c_1 and d_1 are calculated from equation 24 replacing c

by c_2 and d by d_2. With these substitutions equations 29

simplifies to

$$r(c,d,1-3\Delta) = - [G_1(c,d) + G_1(c_1, d_1) + G_1(c_2, d_2)]\Delta$$

$$s(c,d,1-3\Delta) = - [G_2(c,d) + G_2(c_1, d_1) + G_2(c_2, d_2)]\Delta \tag{31}$$

The procedure when extended upto $a = 1 - N$ (that is, $a = 0$), the desired missing initial conditions are obtained.

$$y_1(0) = r(c_0, d_0, 0) = - \sum_{i=0}^{N-1} G_1(c_i, d_i)\Delta$$

$$y_2(0) = s(c_0, d_0, 0) = - \sum_{i=0}^{N-1} G_2(c_i, d_i)\Delta \tag{32}$$

since at $a = 0$; $c = c_0$ and $d = d_0$. The values of $c_2, c_3 \cdots, c_{N-1}$ and $d_2, d_3 \cdots, d_{N-1}$ are calculated from the following relations which are the generalized form of equations 24 and 28.

$$c_I = c - [G_1(c,d) + \sum_{i=1}^{I-1} G_1(c_i, d_i)]\Delta^2$$

$$d_I = d - [G_2(c,d) + \sum_{i=1}^{I-1} G_2(c_i, d_i)]\Delta^2 \tag{33}$$

Where I can take any value from 2 to N. The values of c_i and d_i are to be calculated successively as explained in the procedure given below. However it is to be noted that a new value of c_i and d_i is calculated from the last computed values of c's and d's. As expected the accuracy of the solution increases with increase in the number of increments N or

decrease in the value of increment, but the amount of computation and therefore computation time required for solution is also increased substantially. It can easily be shown that $2 \times (2)^{N-1}$ is the total number of c and d values calculated to get the appropriate values of c's and d's for substitution in equation (32), but the solution is explicit and interpolation or trial and error are not involved.

The computational procedure to get c_5 is explained in Table I, and the procedure is continued upto c_N. The number in parenthesis in the fourth column indicates the step in which a particular value is obtained for substitution. By comparing equations 32 and 33 it can be shown that the missing initial conditions are

$$y_1(0) = (c_N - c_0)/\Delta$$
$$y_2(0) = (d_N - d_0)/\Delta$$

TABLE I

Computational Procedure to Obtain the Value of c_5

Step No.	Quantity Calculated	Equation used	Values substituted in equation	Number of divisions, N
(i)	c_1	24	c_0 for c	1
(ii)	c_2	28	c_0 for c and c_1(i)	2
(iii)	c_1	24	c_2(ii) for c	
(iv)	c_3	33, i=3	c_0 for c, c_1(iii) and c_2(ii)	3
(v)	c_1	24	c_3(iv) for c	
(vi)	c_2	28	c_3(iv) for c and c_1(v)	
(vii)	c_1	24	c_2(vi) for c	
(viii)	c_4	33, i=4	c_0 for c, c_1(vii) c_2(vi) and c_3(iv)	4
(ix)	c_1	24	c_4(viii) for c	
(x)	c_2	28	c_4(viii) for c and c_1(ix)	
(xi)	c_1	24	c_2(x) for c	
(xii)	c_3	33, i=3	c_4(viii) for c, c_1(xi) and c_2(x)	
(xiii)	c_1	24	c_3(xii) for c	
(xiv)	c_2	28	c_3(xii) for c and c_1(xiii)	
(xv)	c_1	24	c_2(xiv) for c	
(xvi)	c_5	33, i=5	c_0 for c, c_1(xv), c_2(xiv), c_3(xii) and c_4(viii)	5

E. Results and Discussion

The method presented in this paper to solve a system of non-linear boundary value equations using invariant imbedding concept is direct involving less computational error and time. Table II gives the values of $y_1(0)$ and $y_2(0)$ obtained by solving equation 13 and 14 with $c_0 = d_0 = 0$.

TABLE II

Missing Initial Conditions $y_1(0)$ and $y_2(0)$ for $c_0 = d_0 = 0$

N	Δ	$y_1(0)$	$y_2(0)$
8	1/8	0.642778	0.432815
9	1/9	0.640918	0.429448
10	1/10	0.639431	0.426793
True value		0.626181	0.404287

The computation was carried out on IBM-7044 and required approximately $1\frac{1}{2}$ seconds for calculation with $\Delta = 0.1$ (N=10). With each increase in the value of N by 1, the amount of time for computation doubles, thus for N=20, the time will be about $\frac{1}{2}$ hour. To save computation time and still get a good accuracy a polynomial equation of the form given below may be used and the final values obtained by substituting $\Delta = 0$.

$$y_1(0) = A_1 + B_1\Delta + C_1 \Delta^2 + \ldots\ldots\ldots$$
$$y_2(0) = A_2 + B_2\Delta + C_2 \Delta^2 + \ldots\ldots\ldots$$

(34)

A three constant polynomial with $y_1(0)$ and $y_2(0)$ values calculated for $\Delta = 1/8$, 1/9 and 1/10 gives the following values for the missing initial conditions.

$$y_1(0) = 0.626124$$
$$y_2(0) = 0.404393$$

These values are very close to the true values which are obtained by the method of trial and error.

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CHAPTER - V

RESULTS AND DISCUSSION

Results are presented in the tabular form in Appendix A-1 through A-29 and the plotted values are shown in Fig. 1 to 29. The following dimensionless variables are studied:

- Modified Thiele parameter, ϕ_M
- Reaction equilibrium constant, K_1
- Ratio of reaction velocity constants, K_2
- $K_A P_o$
- Ratio of diffusivities, D_B/D_A, D_C/D_A, D_D/D_A, D_E/D_A, and
- Ratio of adsorption equilibrium constants, K_B/K_A, K_C/K_A, K_D/K_A and K_E/K_A

The number of variables studied, excluding modified Thiele parameter, are eleven for independent reactions and nine for parallel as well as series reactions. By combining the variables it was possible to reduce the total number of lumped variables to a minimum of six, but this method was not followed because of its inability to present the results in a clearcut way. On the other hand, the variation of these lumped variables (which are function of the variables studied) have little meaning as the variation in one will effect the value of the other. For these reasons, the variables are kept separate in

this study and only one variable is varied at a time. This
is advantageous as it shows clearly the effect of the variation
in one particular variable while all others are kept unchanged.
However, $\emptyset_M$, contains $K_A p_o$ which is also considered as an
independent variable. The inclusion of $K_A p_o$ in $\emptyset_M$ is justified
on the basis that it provides a better picture of the complex
kinetic expressions and a very important generalization is
possible, viz. for values of $\emptyset_M$ greater than five, in general,
the selectivity effect becomes constant and further increase
in $\emptyset_M$ does not change the selectivity of the reactions. Also
selectivity effect for $\emptyset_M$ values of less than 0.2 is, in general,
negligible. The use of lumped variables by many authors [6, 8
and 9] to present activity of porous catalyst for single reaction
is useful since it was possible to reduce the total number of
lumped variables in those simple cases to one or two, in
addition to modified Thiele parameter, and the presentation of
the results was not difficult. A problem can be solved by
finding the values of each of these lumped variables and the
activity value is obtained from the proper curves. With six
lumped variables, in addition to modified Thiele parameter,
at least 729, that is, 3^6 curves are required to present the
effect on selectivity ratio as a function of $\emptyset_M$ for only three
selected values of each of these lumped variables for any
given reaction, obviously a formidable task of doubtful merit.

The effect of diffusion is presented in the form of a dimensionless selectivity ratio, S_R, as a function of modified Thiele parameter, $\emptyset_M$. At a time only one variable is studied and the values of all other variables are kept constant at unity. The range of the values of each of the variables studied is given in Table III.

Table III

Range of the Values of the Variables Studied

Variable	Range
$\emptyset_M$	0.1 – 10.
K_1	0.1 – 100.
K_2	0.1 – 10.
$K_A P_o$	0.01 – 100.
D_B/D_A, D_C/D_A, D_D/D_A, D_E/D_A	0.25 – 4.
K_B/K_A, K_E/K_A	0.25 – 4.
K_C/K_A, K_D/K_A	0.0 – 4.

For clarity of presentation true reaction rate constant and adsorption equilibrium constant are shown separately while defining the reaction rate constant, but the observed reaction rate constant is simply a product of the true surface reaction rate constant and the appropriate adsorption equilibrium constant.

Modified Thiele parameter, ϕ_M, is defined as $L\sqrt{\dfrac{k_1 K_A RT}{D_A(1+K_A p_o)}}$, which is also a function of $K_A p_o$. While studying the effect of variation in the values of $K_A p_o$, the value of modified Thiele parameter also changes. In reporting the results, the variation in modified Thiele parameter due to change in the value of $K_A p_o$ is not considered. However if the net effect on the value of selectivity ratio due to change in the value of $K_A p_o$ is required, the consequent change in ϕ_M (due to change in $K_A p_o$) is to be calculated and the selectivity ratio value is to be obtained at this new value of ϕ_M. In all such cases, the selectivity ratio values are also reported as a function of ordinary Thiele parameter, ϕ, which is defined as $L\sqrt{\dfrac{k_1 K_A RT}{D_A}}$ and is independent of $K_A p_o$. The values of ϕ_M as a function of ϕ are given in Table IV.

Very small values of $K_A p_o$ mean that the modified Thiele parameter becomes nearly equal to ordinary Thiele parameter and the rate equations are nearly simple first or second order provided adsorption equilibrium constants for other components are not large. When one of the product is not adsorbed at all, K_i/K_A for that component is zero. Of special interest is the case for component C. When $K_C/K_A=0$, the component C is not adsorbed at all and reacts in the gas phase only. When the value of reaction equilibrium constant K_1 is greater than ten the reverse reaction is negligible and hence the reaction can be treated as irreversible.

Table IV

Modified Thiele Parameter, ϕ_M, as a Function of Ordinary

Thiele Parameter, ϕ, for Selected Values of $K_A p_o$

$K_A p_o \rightarrow$ $\phi \downarrow$	0.01	0.1	1.	10.	100.
0.1	0.099	0.095	0.071	0.030	0.01
1.	0.995	0.954	0.707	0.302	0.099
10.	9.95	9.54	7.07	3.02	0.995

In all cases except two, the selectivity ratio decreases
with the increase in modified Thiele parameter. Only when the
values of D_E/D_A and of K_2 are less than unity, the selectivity
ratio is found to increase with the increase in modified Thiele
parameter. The change in selectivity ratio continues up to
modified Thiele parameter, ϕ_M, value of nearly five. For values
of ϕ_M greater than five, the selectivity ratio becomes nearly
constant, since at these values most of the reaction is over in
a catalyst pore and further increase in modified Thiele parameter
do not change the product concentration appreciably and therefore
the selectivity ratio approaches a constant value. However,
further increase in the values of ϕ_M will continue to decrease
the activity of the catalyst. The concentration at the end of
the pore has been calculated for parallel reactions for different

values of modified Thiele parameter keeping all other variables
at unity and the results are presented in Table V. It is clear
from the values given in Table V that the percent composition
of reactants A and B for a value of ϕ_M greater than five is
close to zero, while that of the products C and D is nearly
constant.

<p style="text-align:center">Table V</p>

Mole Fractions of Different Components at the Pore End as a
Function of Modified Thiele Parameter,ϕ_M, for Parallel Reactions

ϕ_M	A	B	C	D
1.	0.441	0.060	0.280	0.219
2.	0.171	0.046	0.415	0.368
3.	0.076	0.028	0.461	0.435
4.	0.037	0.016	0.482	0.465
5.	0.019	0.010	0.490	0.481
7.	0.005	0.004	0.498	0.493
10.	0.001	0.001	0.500	0.498

Method of invariant imbedding is used to calculate
selectivity ratio for different values of modified Thiele
parameter up to a value two (in some cases up to a value of
3 also). For values of ϕ_M greater than three, the values of
selectivity ratio obtained by above technique is in error,
because the increment used in computation ($\Delta = 0.1$) is too

large for these conditions. Quasilinearization technique is used to calculate the selectivity ratio for the values of modified Thiele parameter greater than two. This technique also does not converge in some cases for large values of $\phi_M(\phi_M = 10)$ in parallel reactions and for values of ϕ_M greater than three (and in some cases for $\phi_M = 3$ also) in the case of series reactions. The time taken for obtaining one set of values by invariant imbedding technique on IBM 7044 is less than three seconds. The time taken by quasilinearization technique depends upon the type of reaction, the values of the constants, and the accuracy desired. This time varies in these computations from 12 to 60 seconds, which is much larger when compared to 3 seconds required by invariant imbedding technique. The curves are extrapolated in the cases where the solution is not obtained and the extrapolated portion of the curves is shown by dotted lines. No value is reported in the tables for such cases.

A. Independent Reactions

The discussion is based on reactions
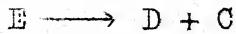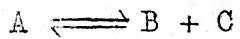
$$A \rightleftharpoons B + C$$

$$E \longrightarrow D + C$$

and the selectivity ratio is defined as the ratio of selectivity with and without diffusion effects. The selectivity is defined as the ratio of the rates of disappearance of reactants A and E, that is, r_A/r_E. For the reaction system considered, the

selectivity without diffusion limitation is equal to K_2.

For irreversible reaction, that is, K_1 greater than ten, if the diffusivities of both the reactants A and E are same and also, if both the reaction rate constants are equal in magnitude, then there is no effect of diffusion, because diffusion limitation will not change the ratio of reactant concentrations, and hence their relative rates. This is shown in Fig.1 for $K_1 = 100$, where the value of selectivity ratio remains nearly unchanged. As the value of K_1 is lowered, the first reaction becomes more and more reversible and the net rate of the first reaction is reduced due to increase in the product concentration as a result of diffusion limitation. However the rate of irreversible reaction is not changed and therefore selectivity ratio is reduced. For highly reversible reactions, the reduction in selectivity ratio is quite significant [Appendix A-1].

When K_2 is varied, the reaction velocity constant for the second reaction is changed. If second reaction is faster than the first and if the component E cannot diffuse equally faster, then the rate of the second reaction does not increase proportionately, since the surface concentration of reactant E keeps on decreasing due to diffusion limitation. Accordingly if the second reaction is slower than the first (K_2 greater than unity), eventhough selectivity is increased but the selectivity ratio is decreased with the increase in modified Thiele
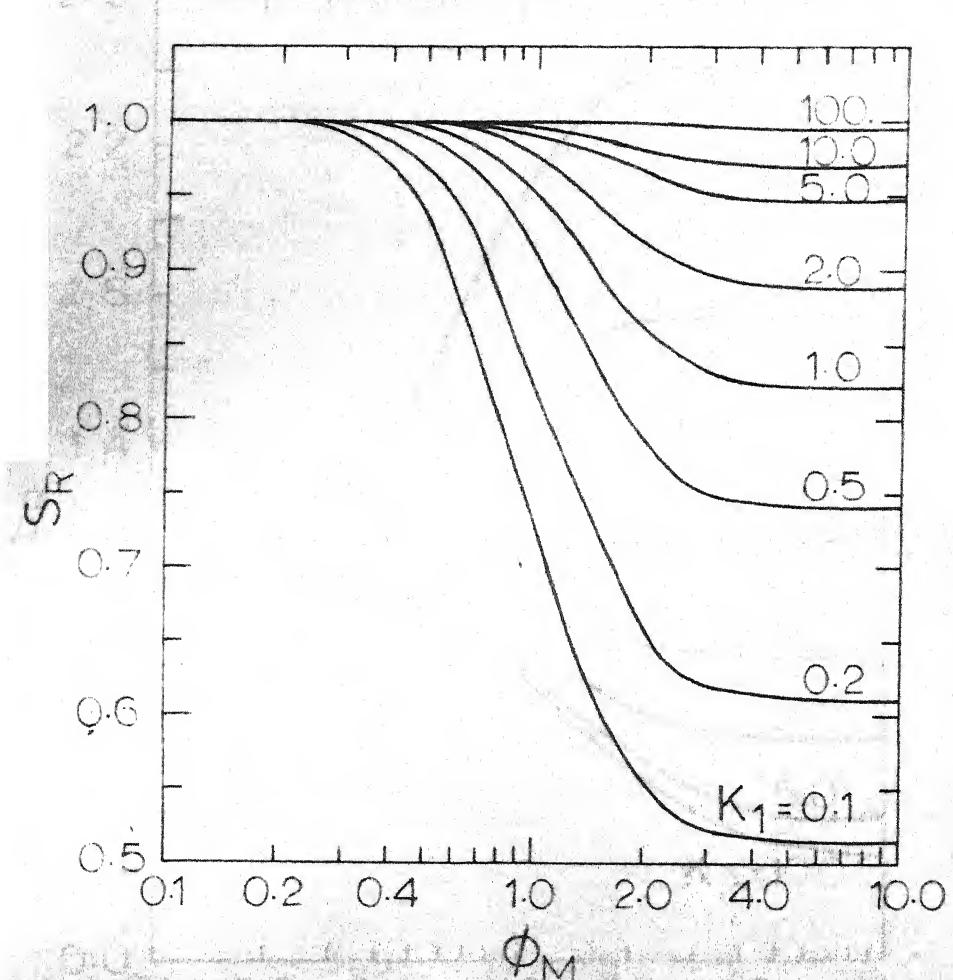
Fig.1 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of K_1.
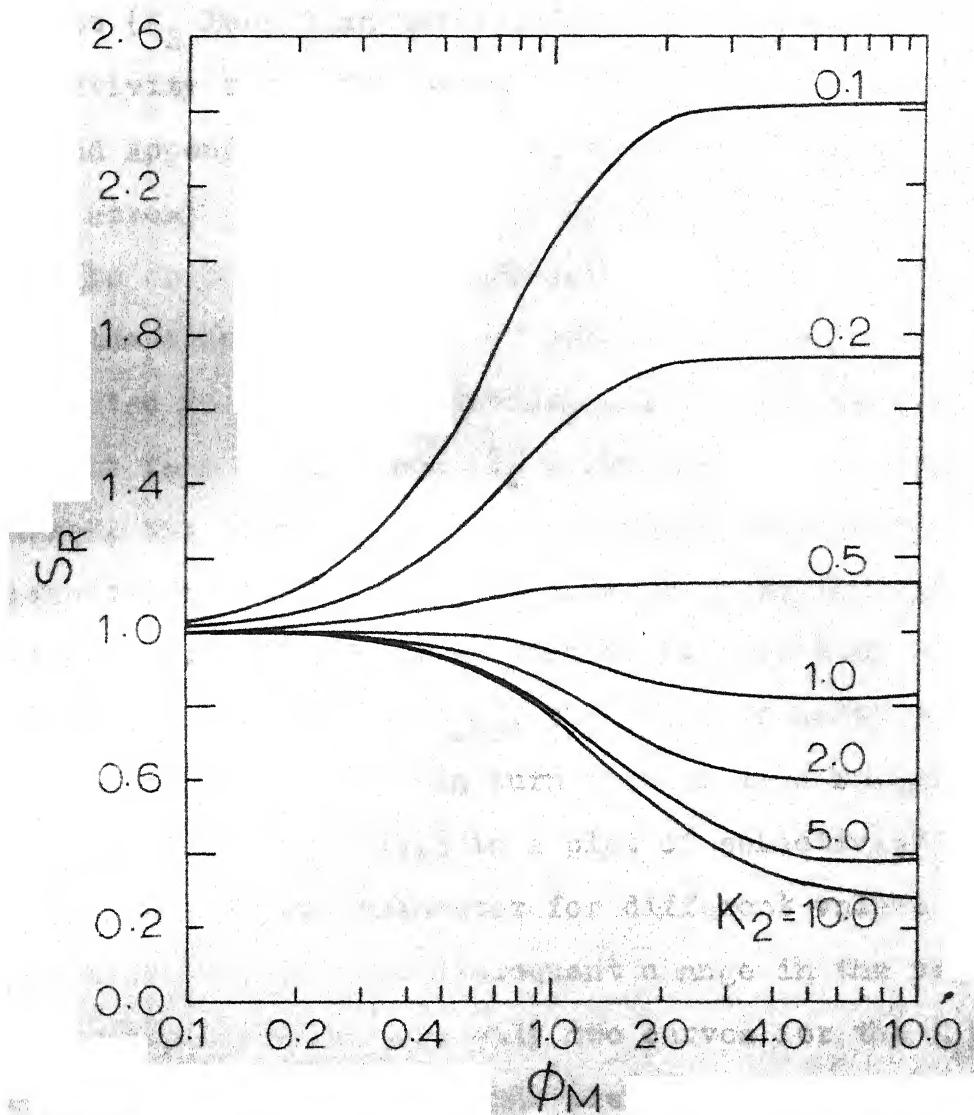
Fig. 2 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of K_2.

parameter, $\emptyset_M$. Conversely, if the second reaction is faster than first (K_2 less than unity), the selectivity decreases but selectivity ratio is increased with the increase in $\emptyset_M$ [Fig.2 and Appendix A-2]. When $K_2 = 0.1$, the value of selectivity ratio in strong diffusion region ($\emptyset_M = 10$) is 2.43. If the reaction is considered to be irreversible (say $K_1 = 100$), with $K_2 = 0.1$ the calculated value of selectivity ratio is 3.04 (not reported in tables). Furthermore, if irreversible reaction with simple rate expressions ($K_1 = 100$ and $K_A p_o = 0.01$) is considered, the calculated value of selectivity ratio is 3.18 (not reported in tables). This value compares favourably with the value of 3.16, reported by Wheeler [4] for such reactions.

At higher values of $K_A p_o$, the value of modified Thiele parameter decreases, which in turn results in a larger value of selectivity ratio. Fig.3 is a plot of selectivity ratio versus modified Thiele parameter for different values of $K_A p_o$ without accounting for the consequent change in the value of $\emptyset_M$. The curves are so close that only two curves for the $K_A p_o$ values of 0.01 and 100. are shown. When presented in this way, ten thousand fold increase in the value of $K_A p_o$ did not alter the value of selectivity ratio by more than two percent [Appendix A-3] The selectivity ratio values are slightly more for higher values of $K_A p_o$. The effect of varying $K_A p_o$ can be seen more clearly, if $(1 + K_A p_o)$ is taken out of the modified Thiele parameter and

the values of selectivity ratio presented as a function of

ordinary Thiele parameter, $\emptyset = L \sqrt{\dfrac{k_1 K_A RT}{D_A}}$, for selected

values of $K_A p_o$, keeping the value of all other variables at unity.
When presented this way [Table VI] the spread between the curves
is increased to a maximum of twenty percent and the selectivity
ratio increases monotonically with increase in the value of $K_A p_o$
at any given value of $\emptyset$. The increase in the value of $K_A p_o$
corresponds to increase in the value of denominator of rate
equations, which results in the decrease in reaction rates. This
is then analogous to lower effective values of Thiele parameter
corresponding to higher selectivity ratio.

Table VI

Selectivity Ratio, S_R, as a Function of Ordinary Thiele Parameter

$\emptyset$, for Selected Values of $K_A p_o$

$\emptyset$ \ $K_A p_o$	0.01	0.1	1.	10.	100.
0.1	1.000	1.000	1.000	1.000	1.000
1.	0.946	0.953	0.982	0.999	1.000
2.	0.847	0.855	0.909	0.990	1.000
3.	0.821	0.824	0.858	0.968	0.999
4.	0.816	0.818	0.838	0.939	0.997
10.	0.815	0.816	0.824	0.842	0.960

When diffusivity of component B or C is increased, the reaction product diffuses faster and therefore the concentration of product molecules are lowered. Consequently the net rate of first reaction is increased which results in an increase in selectivity ratio [Fig.4 and 5 and Appendix A-4 and A-5].

The effect of changing the diffusivity of component D is negligible as a sixteen fold change in D_D/D_A changes selectivity ratio only slightly. This is because the second reaction is irreversible and the concentration of component D has little effect on the reaction rates [Fig. 6]. Decrease in the diffusivity of component D increases its concentration,. thus lowering the rates of reaction due to the increase in the value of denominator in rate equations. This effect is then analogous to the effect of decrease in the value of ϕ_M, that is, lower values of D_D/D_A results in higher values of selectivity ratio [Appendix A-6].

The effect of changing diffusivity of reactant E with respect to reactant A [Fig.7 and Appendix A-7] is similar to that of K_2 as shown in Fig.2. When the diffusivity of component E is large, the decrease in concentration along the pore will be small, and hence the rate of second reaction will increase resulting in the decrease in selectivity ratio.

When the value of adsorption equilibrium constant for reaction products B, C or D are increased, the selectivity ratio increases. Since increase in the value of adsorption
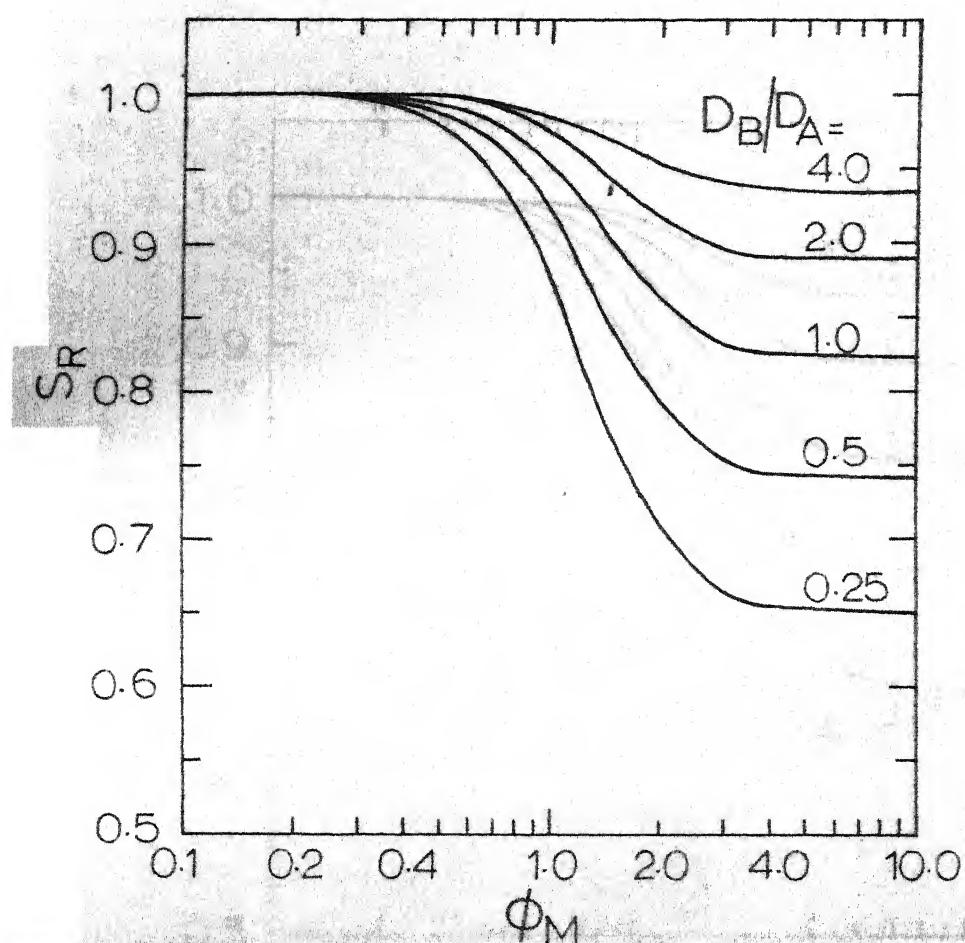
Fig. 4 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_B/D_A.
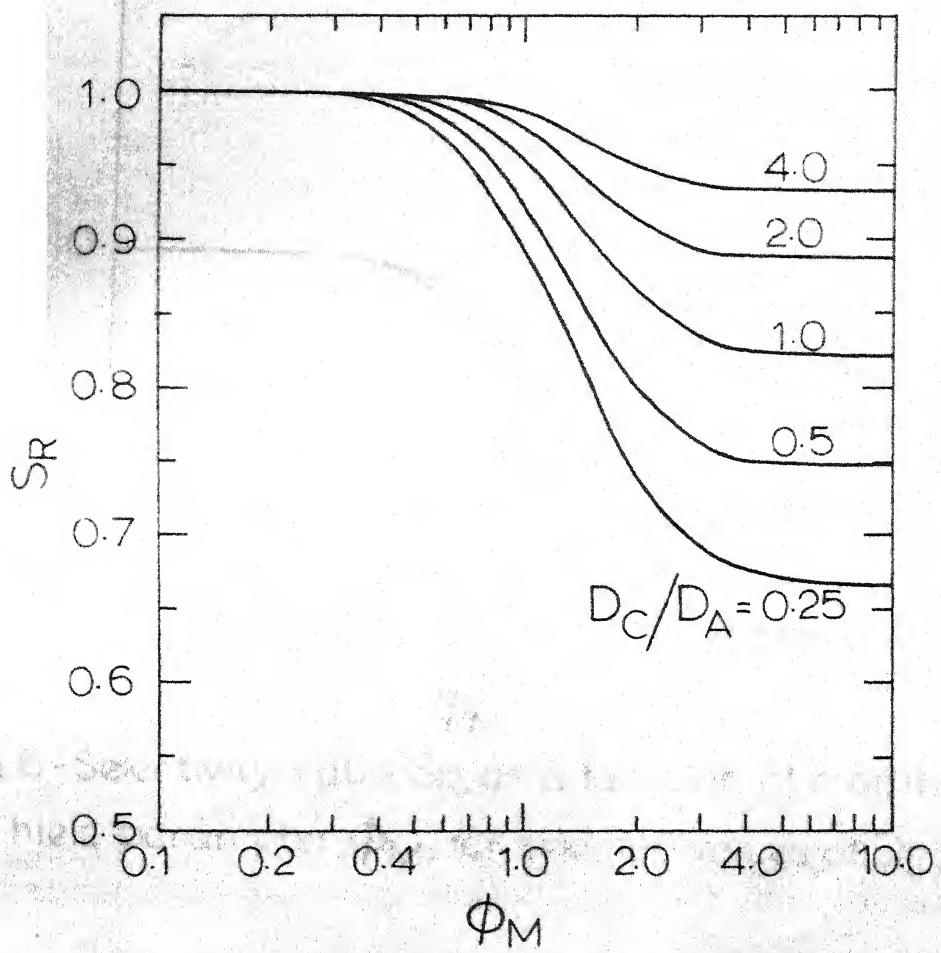
Fig. 5 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_C/D_A.
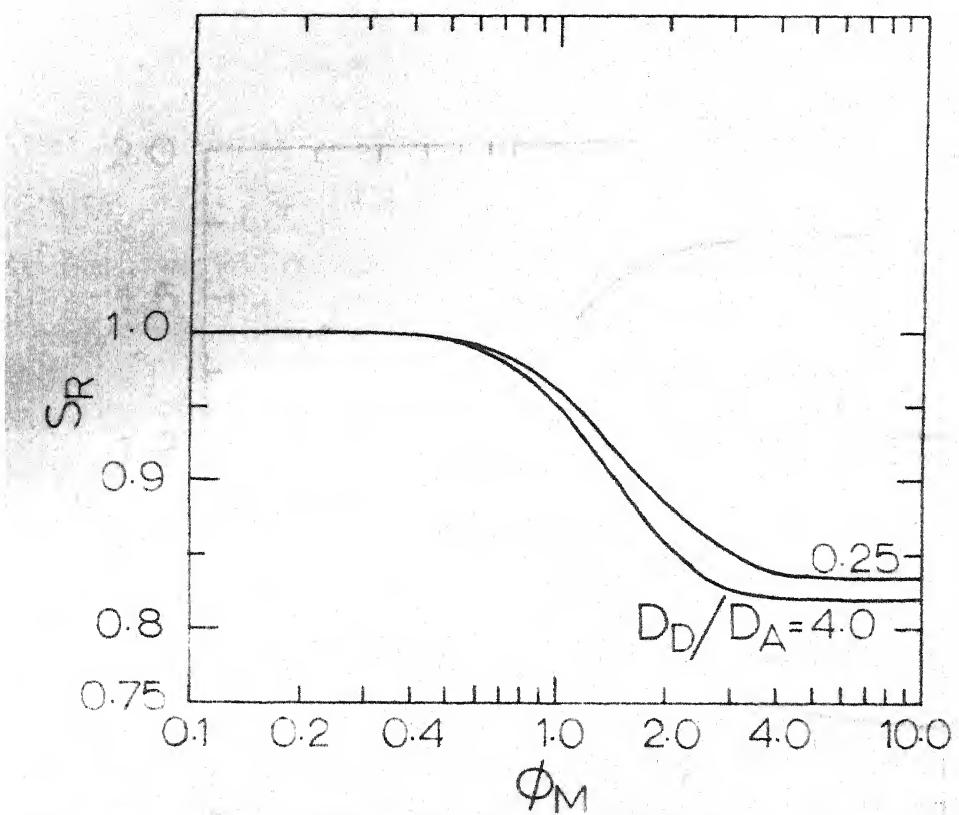
Fig.6 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_D/D_A.
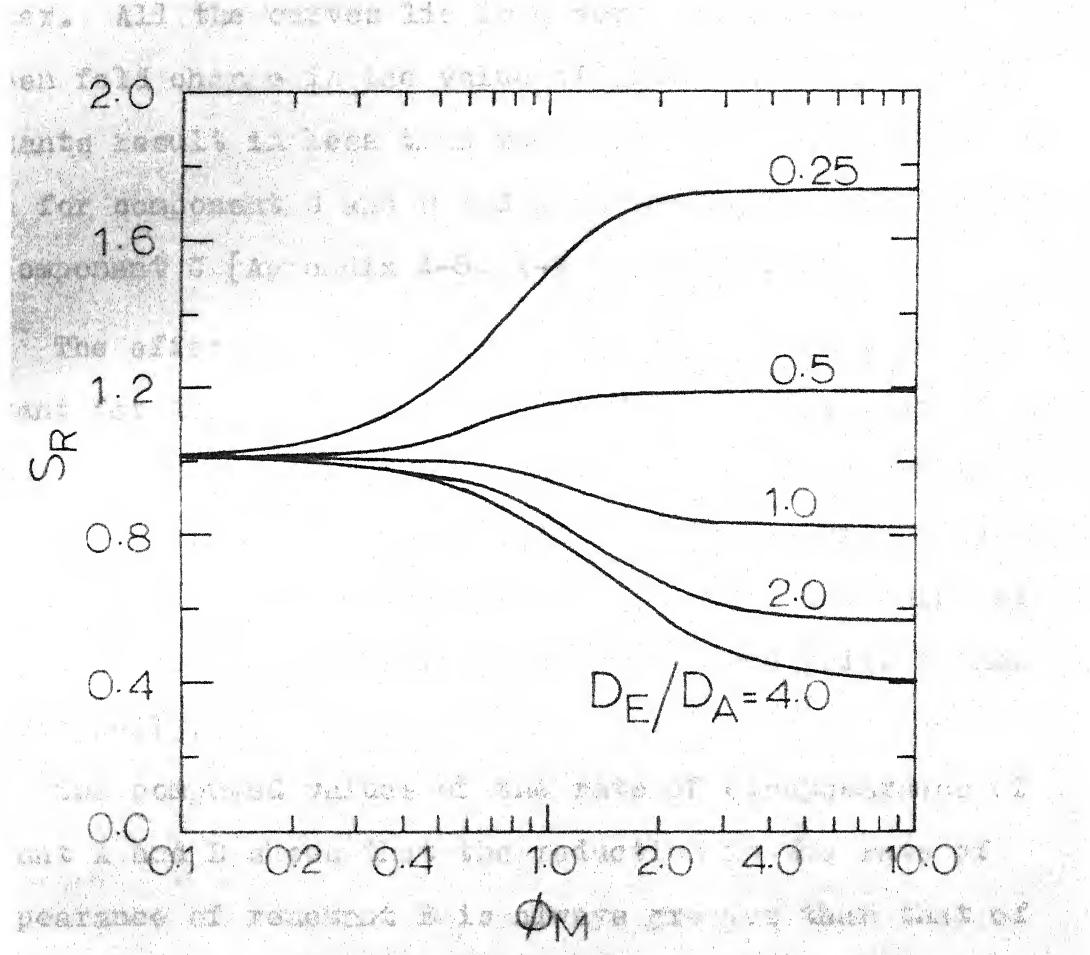
Fig.7-Selectivity ratio, S_R, as a function of modified Thiele parameter, Φ_M, for selected values of D_E/D_A.

equilibrium constants increases the value of the denominator which in turn decreases the rate of reactions and consequently increases the selectivity ratio [Fig. 8, 9, and 10] as explained earlier. All the curves lie in a very narrow band and the sixteen fold change in the value of adsorption equilibrium constants result in less than two percent change in selectivity ratio for component B and D and a maximum change of three percent for component C [Appendix A-8, A-9 and A-10].

The effect of changing the value of adsorption equilibrium constant for the reactant component E is same as that of product component B, C and D for lower values of modified Thiele parameter that is, for higher values of K_E/K_A the selectivity ratio is larger. However, the effect is reversed when the value of modified Thiele parameter is greater than two [Fig. 11 and Appendix A-11].

The computed values of the rate of disappearance of reactant A and E shows that the reduction in the rate of disappearance of reactant E is always greater than that of reactant A as the value of K_B/K_A, K_C/K_A or K_D/K_A increases from 0.25 to 4.0 for all values of $\emptyset_M$. However, this trend is found to be valid while varying K_E/K_A from 0.25 to 4.0 only upto a modified Thiele parameter value of less than two. For higher values of Thiele parameter with increase in the value of K_E/K_A, the reduction in the rate of disappearance of
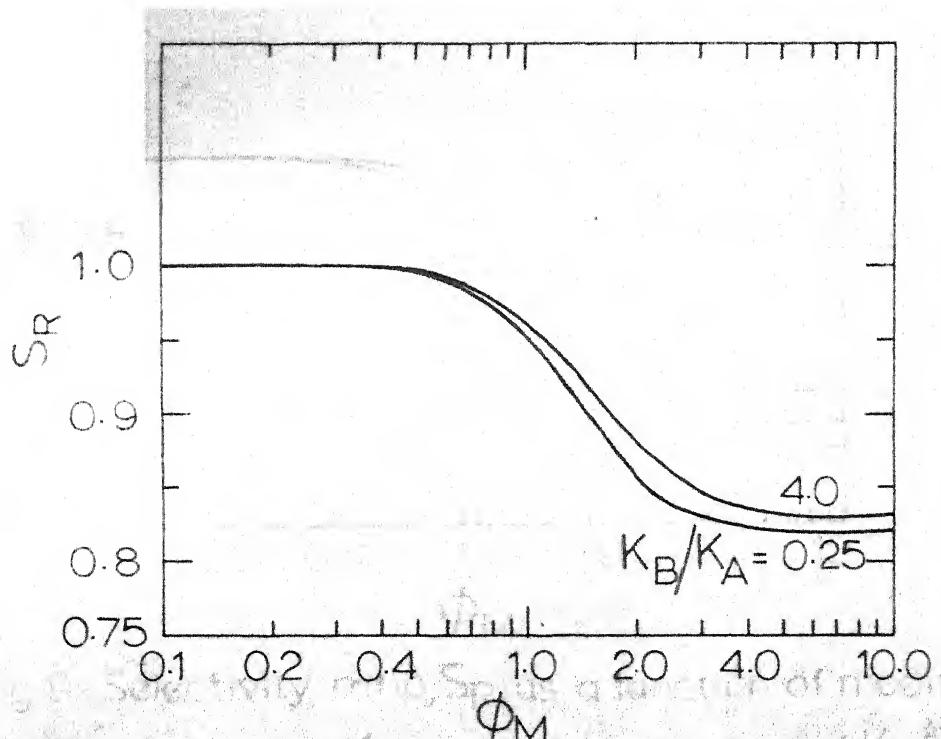
Fig.8-Selectivity ratio, S_R, as a function of modified

Thiele parameter, ϕ_M, for selected values of K_B/K_A.
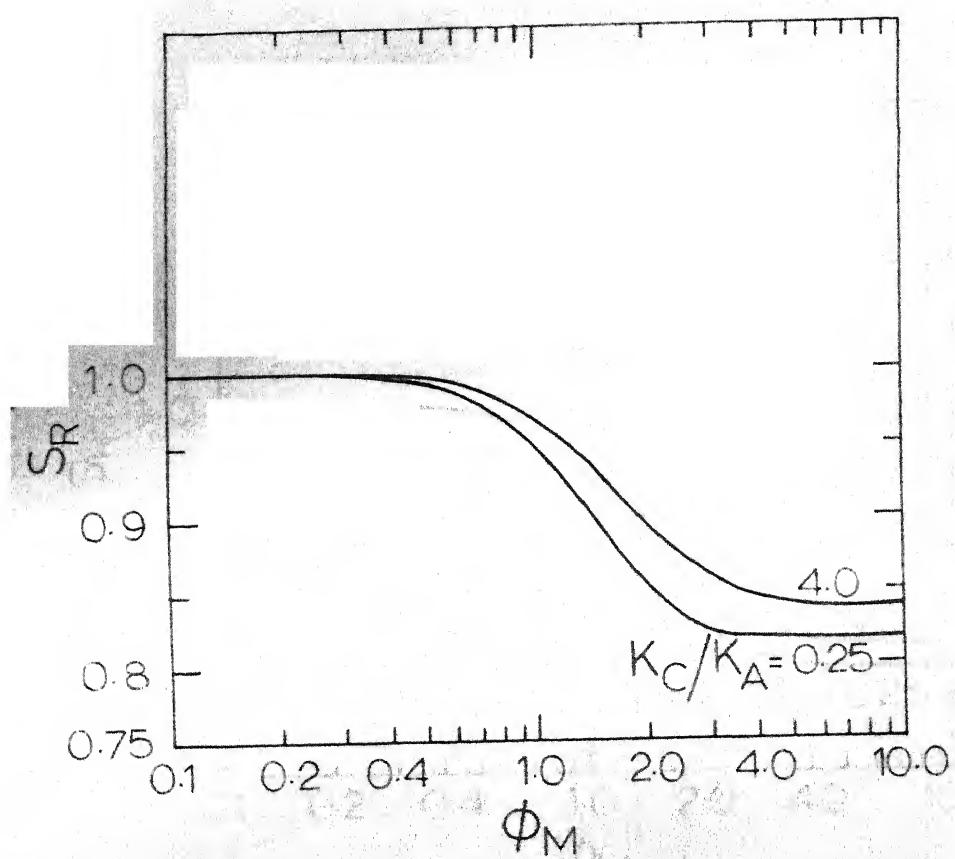
Fig.9-Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of K_C/K_A.
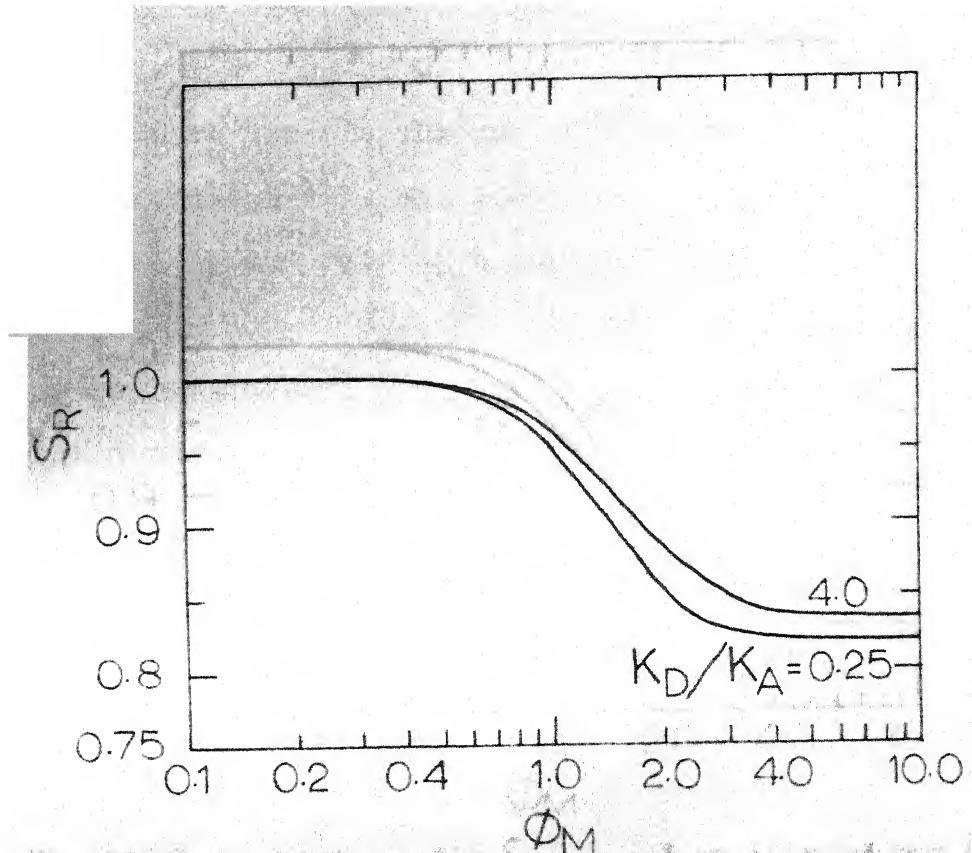
Fig.10 - Selectivity ratio, S_R, as a function of modified
Thiele parameter, Φ_M, for selected values of K_D/K_A.
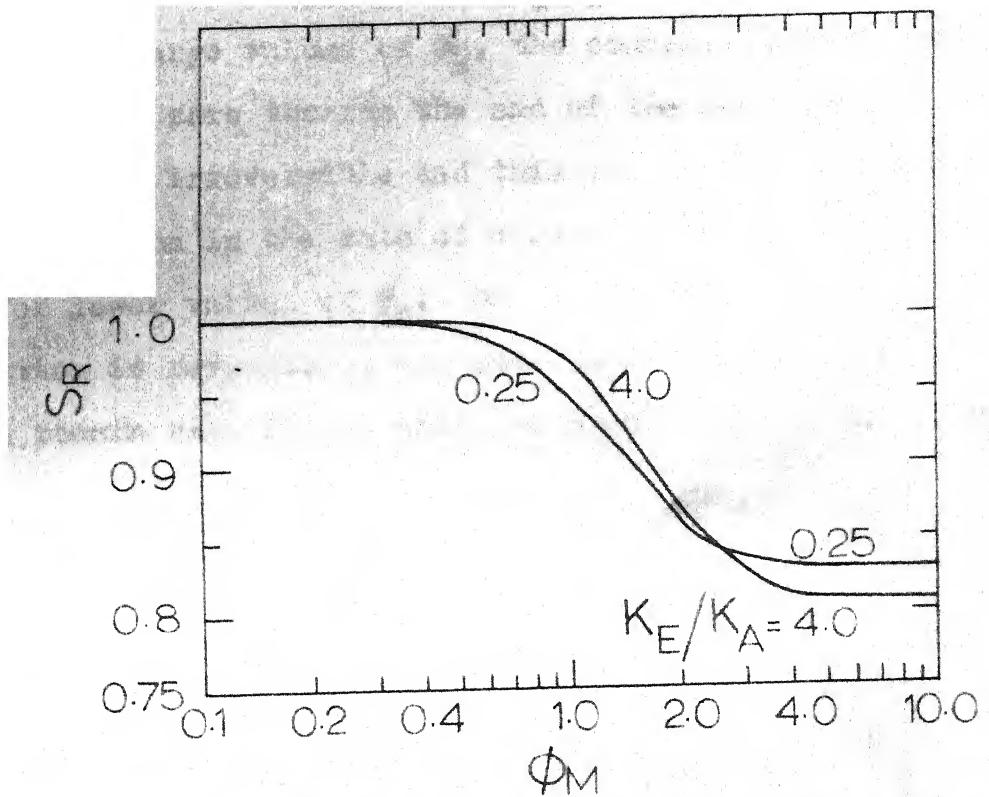
Fig. 11 - Selectivity ratio, S_R, as a function of modified Thiele parameter, Φ_M, for selected values of K_E/K_A.

reactant A is greater than that of reactant E, and this reversal is then responsible for the decrease in the selectivity ratio with increase in the value of K_E/K_A for $\emptyset_M$ values greater than two. For large values of $\emptyset_M$, the concentration of reactant E is close to zero towards the end of the pore because second reaction is irreversible and this is probably responsible that the reduction in the rate of disappearance of E is not as large as for lower values of $\emptyset_M$. On the contrary, since the first reaction is reversible, the reduction in rate of disappearance of A remain significant with increase in the value of K_E/K_A.

B. Parallel Reactions

The discussion is based on the reactions
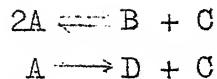
$$2A \rightleftharpoons B + C$$
$$A \longrightarrow D + C$$

and the selectivity ratio is defined as the ratio of selectivity with and without diffusion effects. The selectivity is defined as the ratio of the rate of formation of product B to that of disappearance of reactant A, that is, $r_B/(-r_A)$. For the reaction system considered, the selectivity without diffusion limitation is equal to $K_2 \times K_A p_0/(1+K_A p_0(1+2K_2))$.

The variables studied for parallel reactions are same as listed in Table III except that the component E is not present.

When the first reaction is highly reversible corresponding to low values of equilibrium constant K_1, selectivity ratio is decreased due to rapid increase in the concentration of products C and D as a result of diffusion limitation. The concentration of component B is first increased and then starts decreasing as more and more reactant A is converted to products C and D to maintain the equilibrium of first reaction. Thus for a given value of Thiele parameter as the value of K_2 is lowered the rate of formation of B decreases rapidly while that of D increases slightly due to diffusion limitations. This results in the decrease of selectivity with diffusion limitations, which results in lower values of selectivity ratio [Fig. 12 and Appendix A-12].
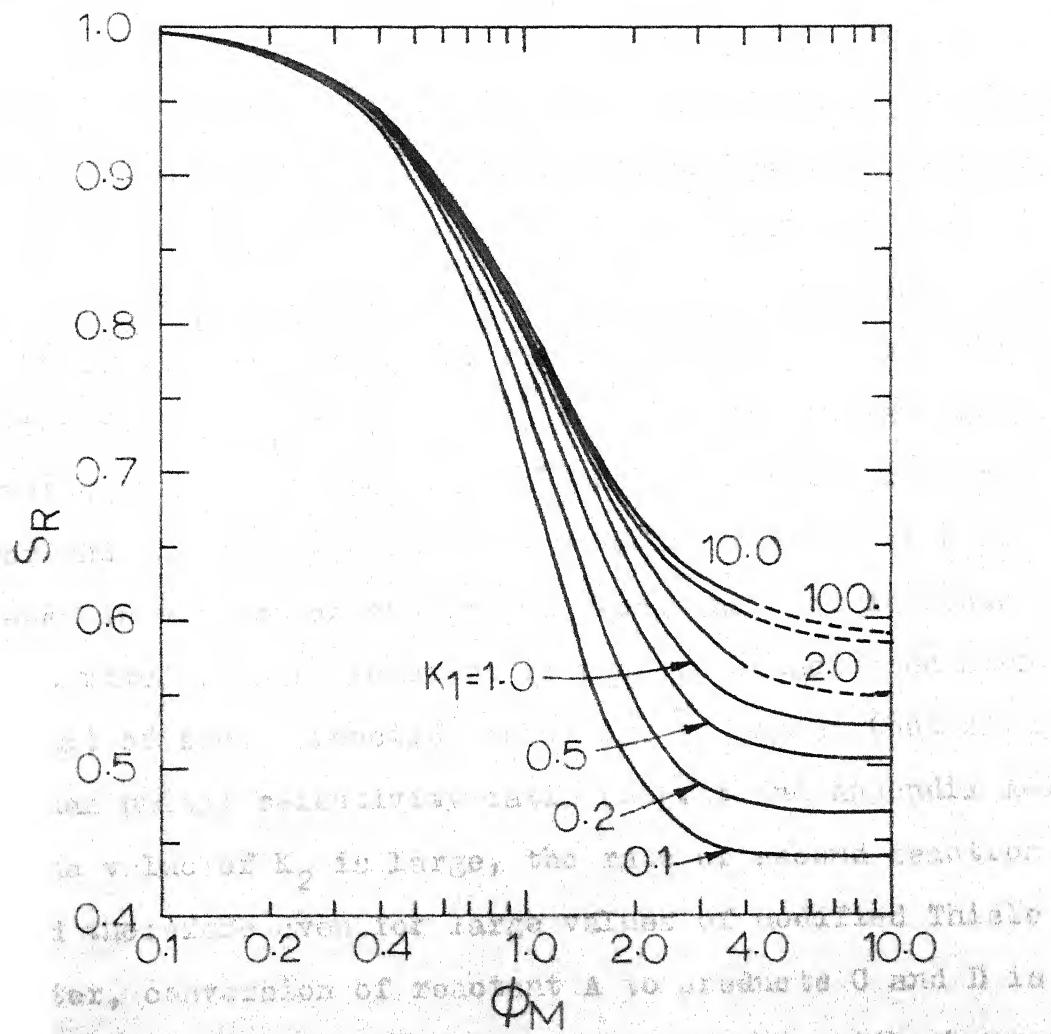
Fig.12-Selectivity ratio,S_R, as a function of modified Thiele parameter,ϕ_M, for selected values of K_1.

For a given value of $\emptyset_M$ the change in K_2 implies the change in the value of rate constant for the second reaction without effecting the value of the rate constant for first reaction. When the value of K_2 is decreased, the rate of second reaction is increased which decreases the reactant concentration and increases the product concentration much more. The net rate of first reaction is therefore reduced much more (since it is second order reversible reaction) than that of second reaction resulting in lower selectivity ratio. Conversely, if the value of K_2 is increased, the second reaction becomes slower and the decrease in reactant concentration as well as increase in product concentration along the pore is reduced. The net rate of first reaction is therefore increased much more than that of second reaction resulting in higher (but always less than unity) selectivity ratio [Fig.13 and Appendix A-13]. When the value of K_2 is large, the rate of second reaction is low and therefore even for large values of modified Thiele parameter, conversion of reactant A to products C and D is not complete and concentration profile changes with change in the value of $\emptyset_M$. As a result of this, the value of selectivity ratio does not become constant for $\emptyset_M$ as large as ten, when K_2 is greater than two. However when second reaction is very fast the conversion of reactant A to products C and D is achieved for values of $\emptyset_M$ as low as four ($K_2 = 0.1$) and further increase in $\emptyset_M$ does not alter the value of S_R significantly.
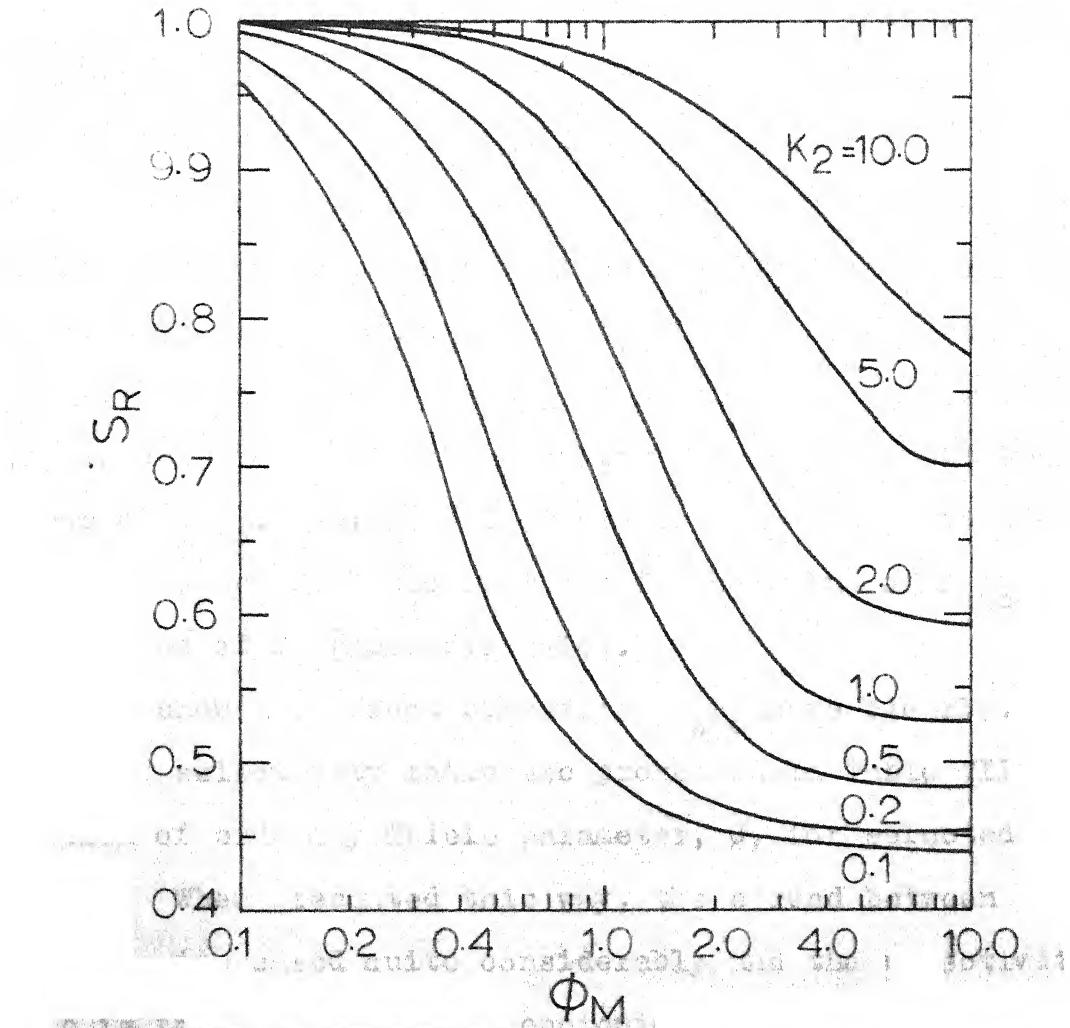
Fig. 13 - Selectivity ratio, S_R, as a function of modified

$K_A p_o$ effects the rate equations in three ways. This appears as a coefficient in the rate equation for first reaction, in modified Thiele parameter and in the denominator of the rate equations. Fig. 14 is a plot of selectivity ratio versus modified Thiele parameter for different values of $K_A p_o$ without considering the effect of the variation of $K_A p_o$ on $\emptyset_M$. When presented this way ten thousand fold increase in the value of $K_A p_o$ alters the value of selectivity ratio to a maximum of twenty percent at a $\emptyset_M$ value of ten. Furthermore, the value of selectivity ratio are slightly higher for low values of $\emptyset_M$ and $K_A p_o$ in comparasion to those at low values of $\emptyset_M$ but large values of $K_A p_o$. For $\emptyset_M$ values greater than one, the selectivity ratio increases with the increase in the value of $K_A p_o$ at any given value of $\emptyset_M$ [Appendix A-14].

To show the effect of varying $K_A p_o$ more clearly, the values of selectivity ratio are presented in Table VII as a function of ordinary Thiele parameter, $\emptyset$, for selected values of $K_A p_o$. When presented this way, the spread between the curves is increased quite considerably and the selectivity ratio is found to increase monotonically with increase in the value of $K_A p_o$ at any given value of $\emptyset$.

The selectivity ratio values for ordinary as well as modified Thiele parameter greater than three and for $K_A p_o$ value of 0.1 are not conforming the general trend as can be seen from Table VII and Appendix A-14. No particular reason for this peculiar behaviour is evident.

Fig.14-Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of $K_A p_0$.

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Table VII

Selectivity Ratio, S_R, as a Function of Ordinary
Thiele Parameter, $\emptyset$, for Selected Values of $K_A p_o$.

$K_A p_o$ $\rightarrow$ / $\emptyset$ $\downarrow$	0.01	0.1	1.	10.	100.
0.1	0.997	0.997	0.998	1.000	1.000
1.	0.777	0.788	0.864	0.965	0.996
2.	0.567	0.591	0.709	0.897	0.984
3.	0.513	0.518	0.618	0.830	0.966
4.	0.498	0.494	0.573	0.773	0.945
10.	0.485	–	0.531	0.617	0.815
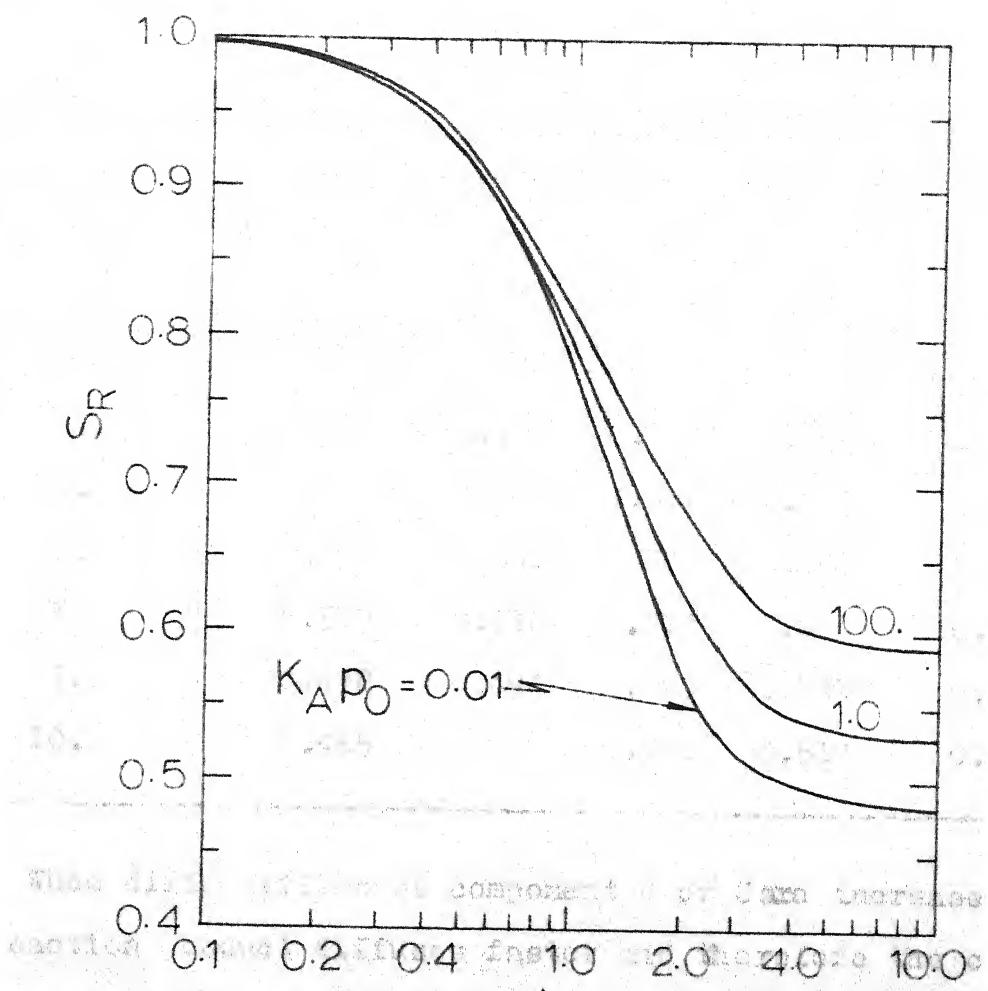
When diffusivities of component B or C are increased
the reaction product diffuses faster and therefore the con-
centration of the product molecules is lowered. This results
in lowering the reaction rate of the reversible step and there-
fore the net rate of first reaction is increased, resulting in
an increase in selectivity ratio [Fig.15, 16 and Appendix A-15
and A-16].

The effect of changing the diffusivity of component D
is negligible [Fig.17 and Appendix A-17] and the small difference
observed in the values is due to the change in the value of the
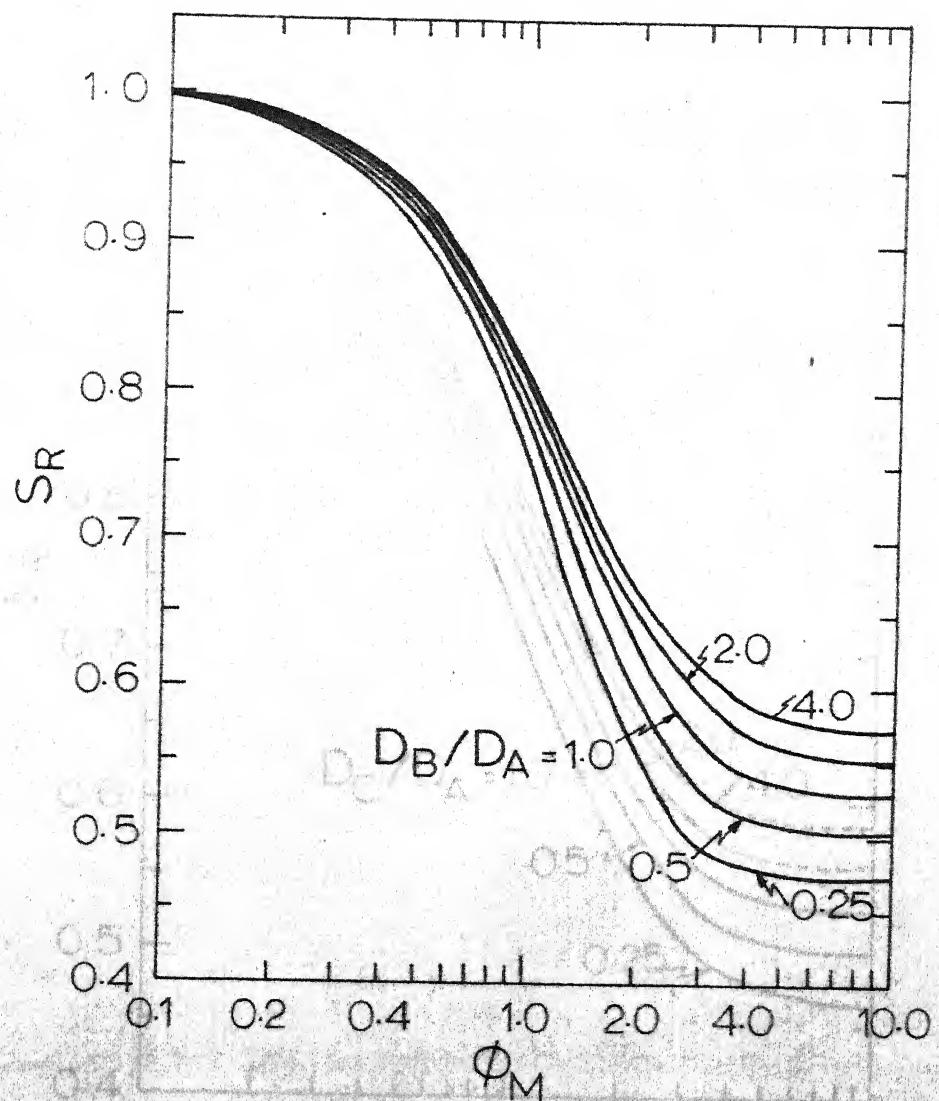
Fig.15 – Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_B/D_A.

Fig.16 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_C/D_A.
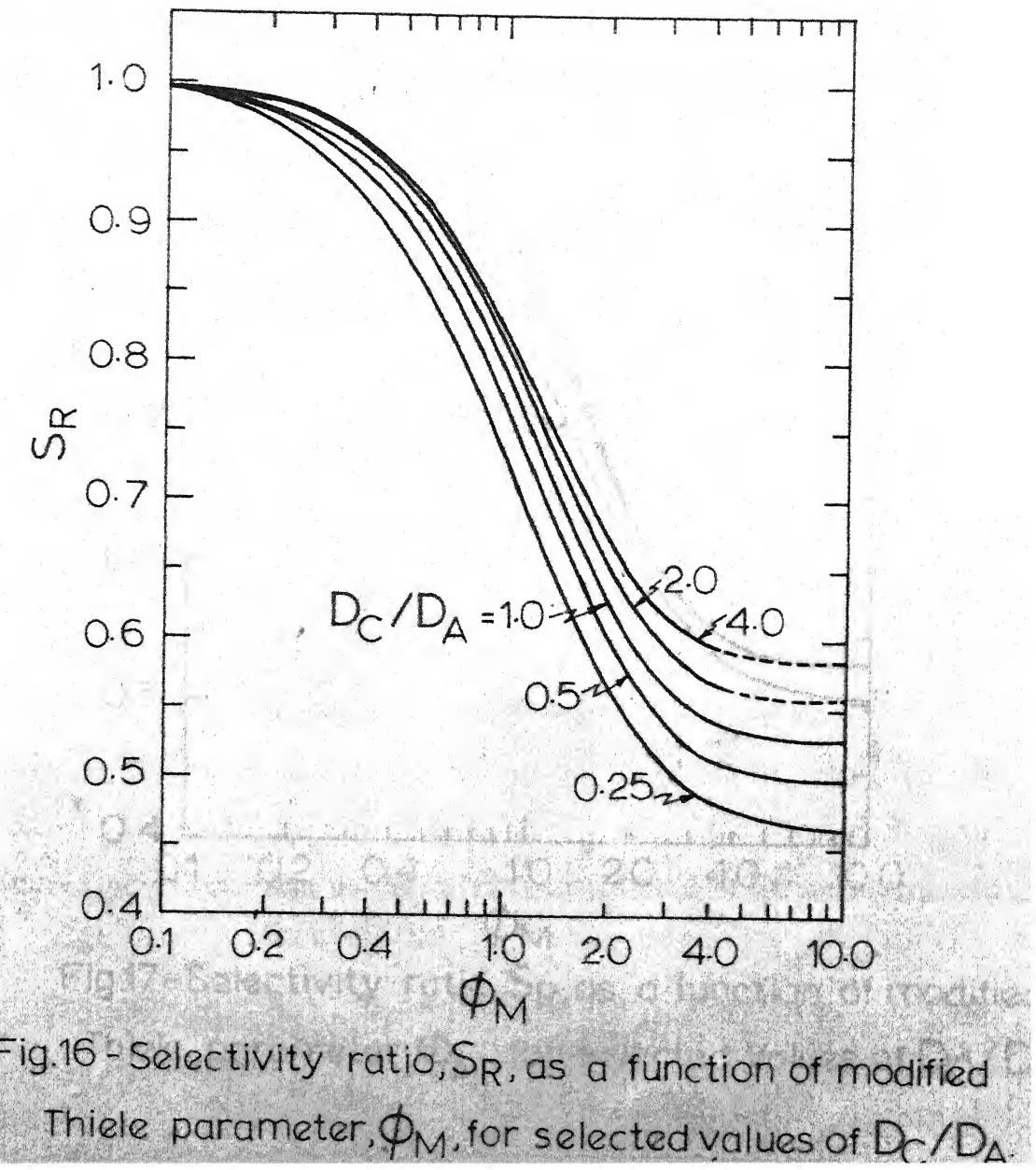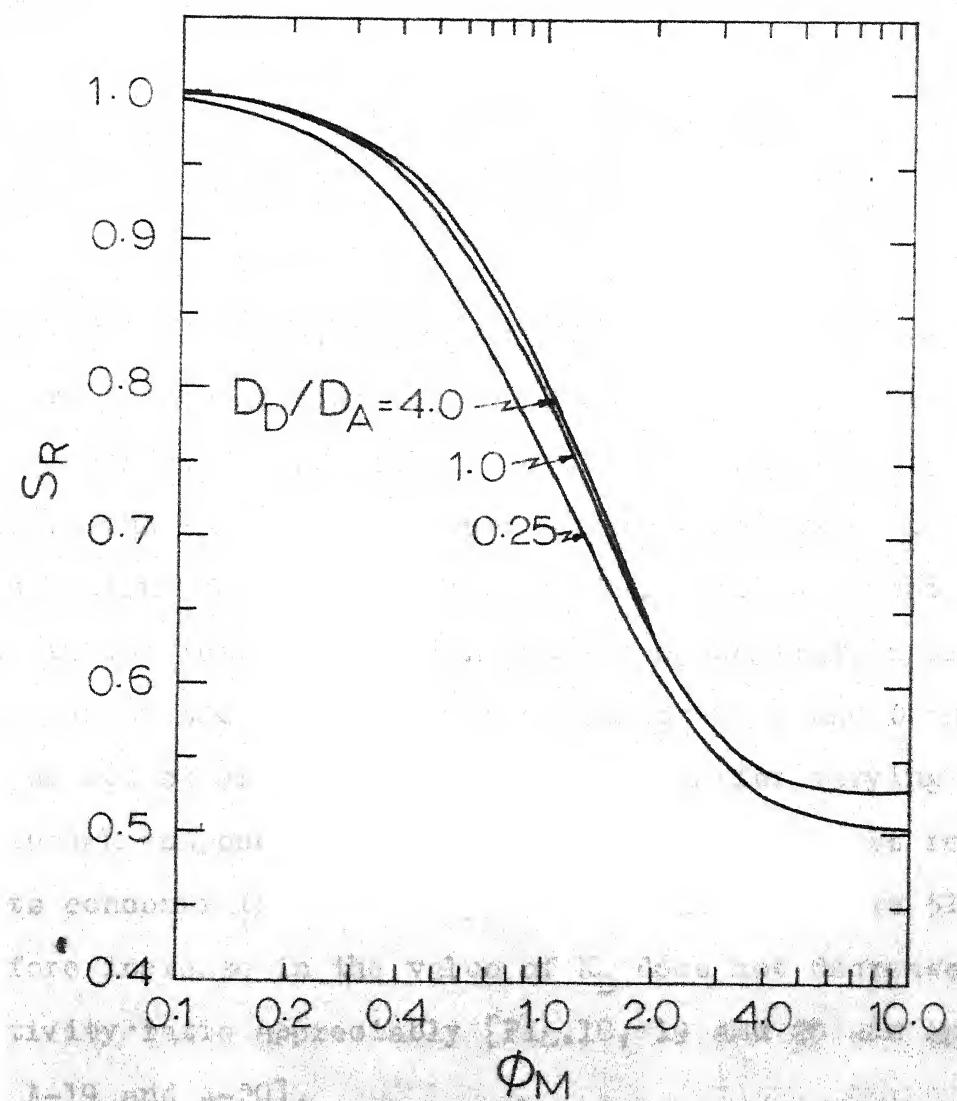
Fig.17 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_D/D_A.

denominator of the rate equations as a result of the change in
the value of D_D/D_A. The effect is similar to that reported for
independent reactions.

The effect of increasing the value of adsorption equilibrium
constant for reaction products B, C or D is to increase the
value of denominator of the rate equations. The reaction rates
are therefore reduced, but the reduction for first reaction is
much more in comparision to second reaction, since it is a second
order reaction. Consequently the value of selectivity ratio is
lowered. The spread in the curves is maximum when K_C is varied
and is minimum for the variation in K_B. The component C parti-
cipate in the reverse reaction and its concentration is equal
to the sum of the concentration of component B and D and there-
fore the effect of varying K_C is more than for varying K_B or K_D.
Even though component B also participates in reverse reaction,
but its concentration is always small [Table V, page 51] and
therefore increase in the value of K_B does not decrease the
selectivity ratio appreciably [Fig.18, 19 and 20 and Appendix
A-18, A-19 and A-20].

The curves for K_i/K_A values of zero are close to those
for K_i/K_A values of 0.25. It is interesting to note that the
rate equations reduce to simple first and second order when
K_D/K_A equals to zero and all other ratios of diffusivities and
adsorption equilibrium constants are unity.
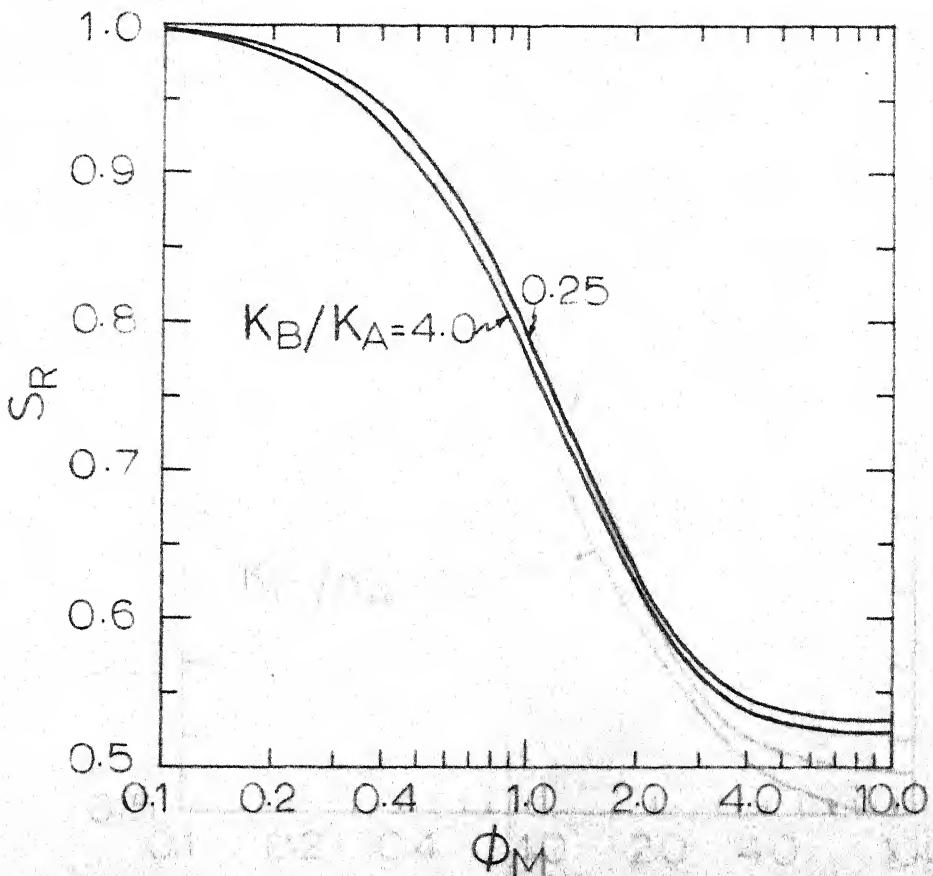
Fig.18 -Selectivity ratio, S_R, as a function of modified Thiele parameter, Φ_M, for selected values of K_B/K_A.
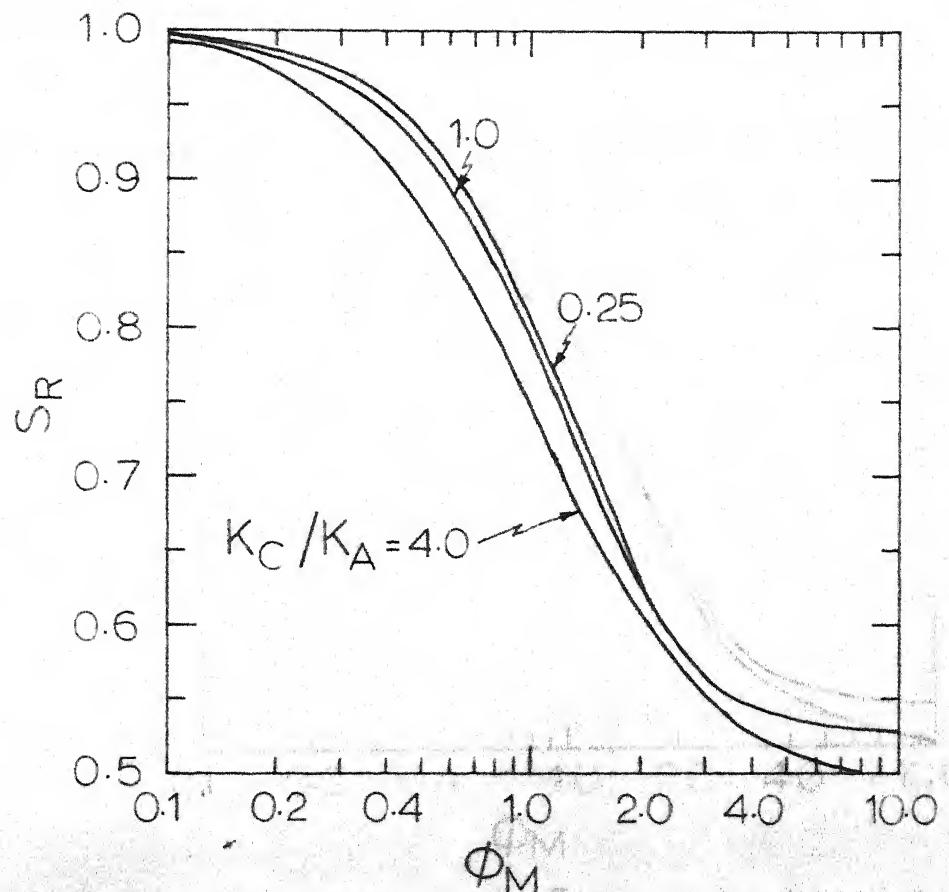
Fig.19–Selectivity ratio, S_R, as a function of modified
Thiele parameter, ϕ_M, for selected values of K_C/K_A.
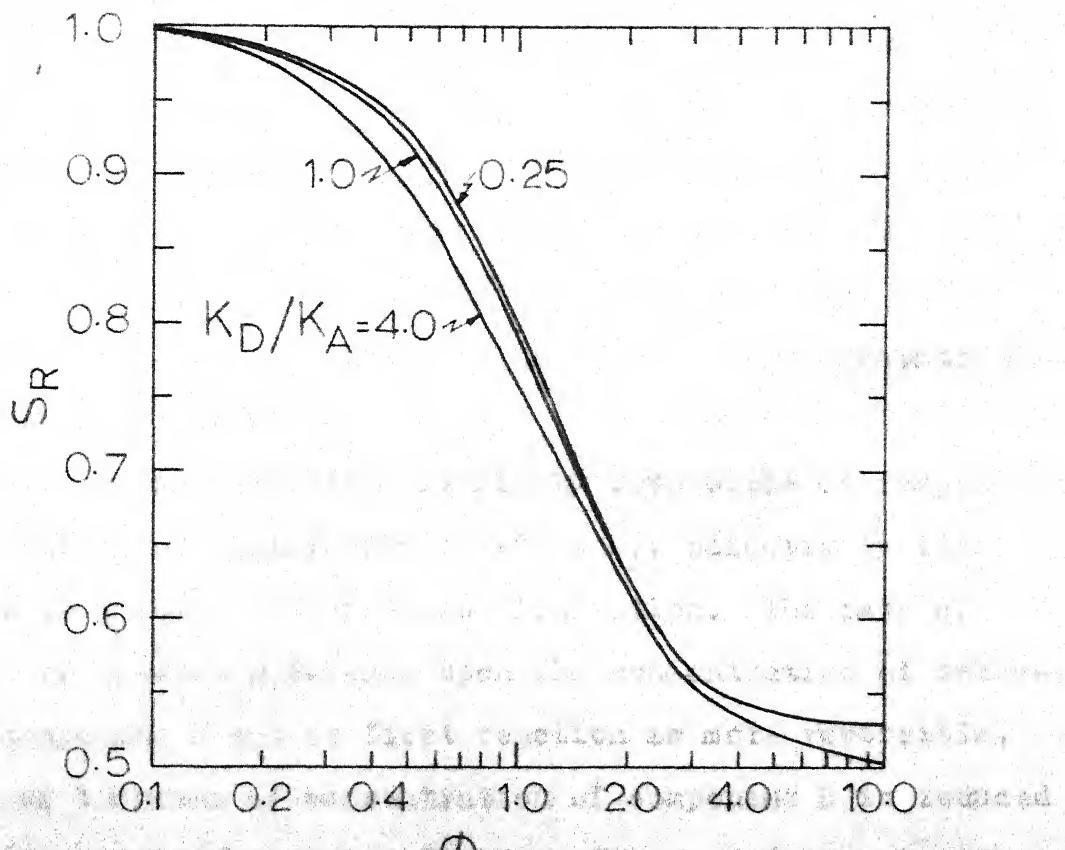
Fig. 20 - Selectivity ratio, S_R, as a function of modified Thiele parameter, Φ_M, for selected values of K_D/K_A

C. Series Reactions

The discussion is based on reactions
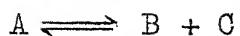
$$A \rightleftharpoons B + C$$

$$B \longrightarrow D + C$$

and the selectivity ratio is defined as the ratio of selectivity with and without diffusion effects. The selectivity is defined as the ratio of the rate of formation of B to that of disappearance of A, that is, $r_B/-r_A$. For the reaction system considered, the selectivity without diffusion limitation is unaffected by any of the variable discussed below, since the product concentration at the pore month is zero.

When the first reaction is highly reversible corresponding to lower values of equilibrium constant K_1, selectivity ratio increased as a result of diffusion limitation. The rate of formation of product D depends upon the concentration of intermediate component B and as first reaction is more reversible, the rate of increase of concentration of component B is reduced in diffusion limited region. The net effect of decreasing the value of K_1 at a given value of modified Thiele parameter is to reduce the rate of formation of component D much more than that of component B. Therefore the selectivity with diffusion limitations is increased which corresponds to higher values of selectivity ratio [Fig. 21 and Appendix A-21].
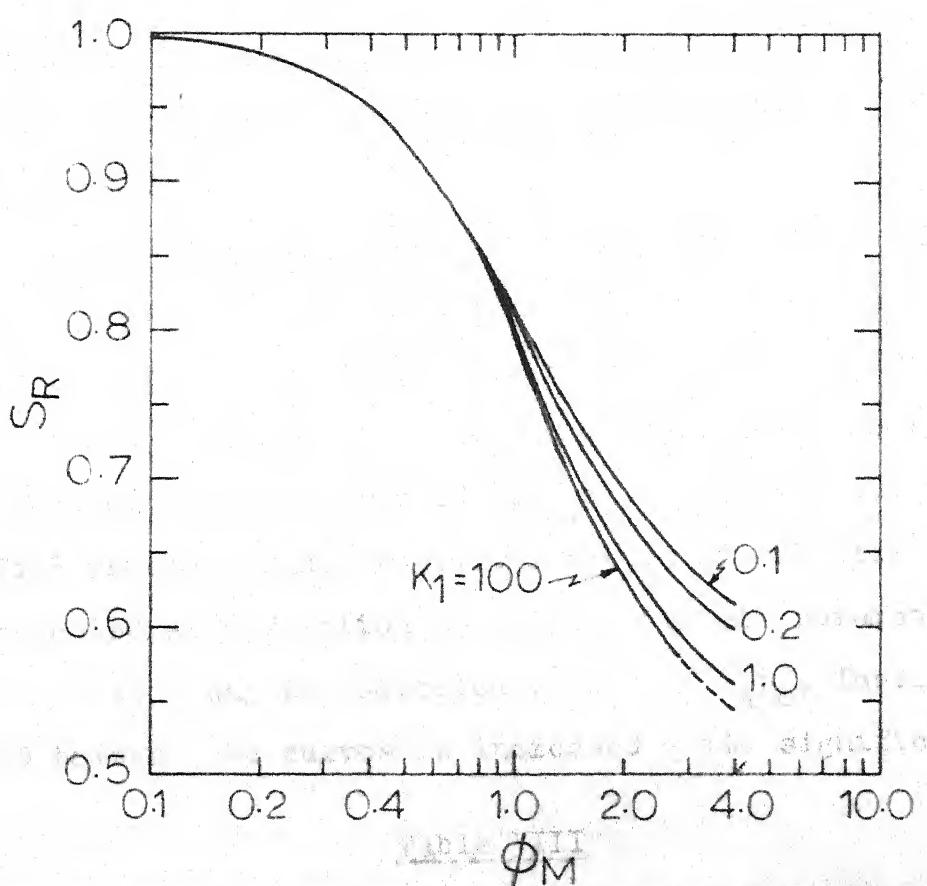
Fig.21-Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of K_1.

When the second reaction is faster, than the first, corresponding to low values of K_2, the intermediate product B is converted to product D at a much rapid rate and therefore the selectivity with diffusion limitation is decreased which corresponds to low values of selectivity ratio [Fig. 22 and Appendix A-22].

Fig. 23 [Appendix A-23] gives the value of selectivity ratio as a function of modified Thiele parameter for selected values of $K_A p_o$. The selectivity ratio is increased with increase in the value of $K_A p_o$ for any value of ϕ_M. The effect of varying $K_A p_o$ becomes more apparent if $(1+K_A p_o)$ is taken out of the modified Thiele parameter and the values of selectivity ratio is presented as a function of ordinary Thiele parameter. When presented this way for selected values of $K_A p_o$, Table VIII, the spread between the curves is increased quite significantly.

Table VIII

Selectivity Ratio, S_R, as a Function of Ordinary Thiele Parameter, ϕ, for Selected Values of $K_A p_o$

| ϕ \ $K_A p_o \rightarrow$	0.01	0.1	1.	10.	100.
0.1	0.997	0.997	0.998	1.000	1.000
1.	0.782	0.798	0.877	0.972	0.997
2.	0.601	0.619	0.720	0.908	0.987
3.	0.555	0.560	0.636	0.838	0.973
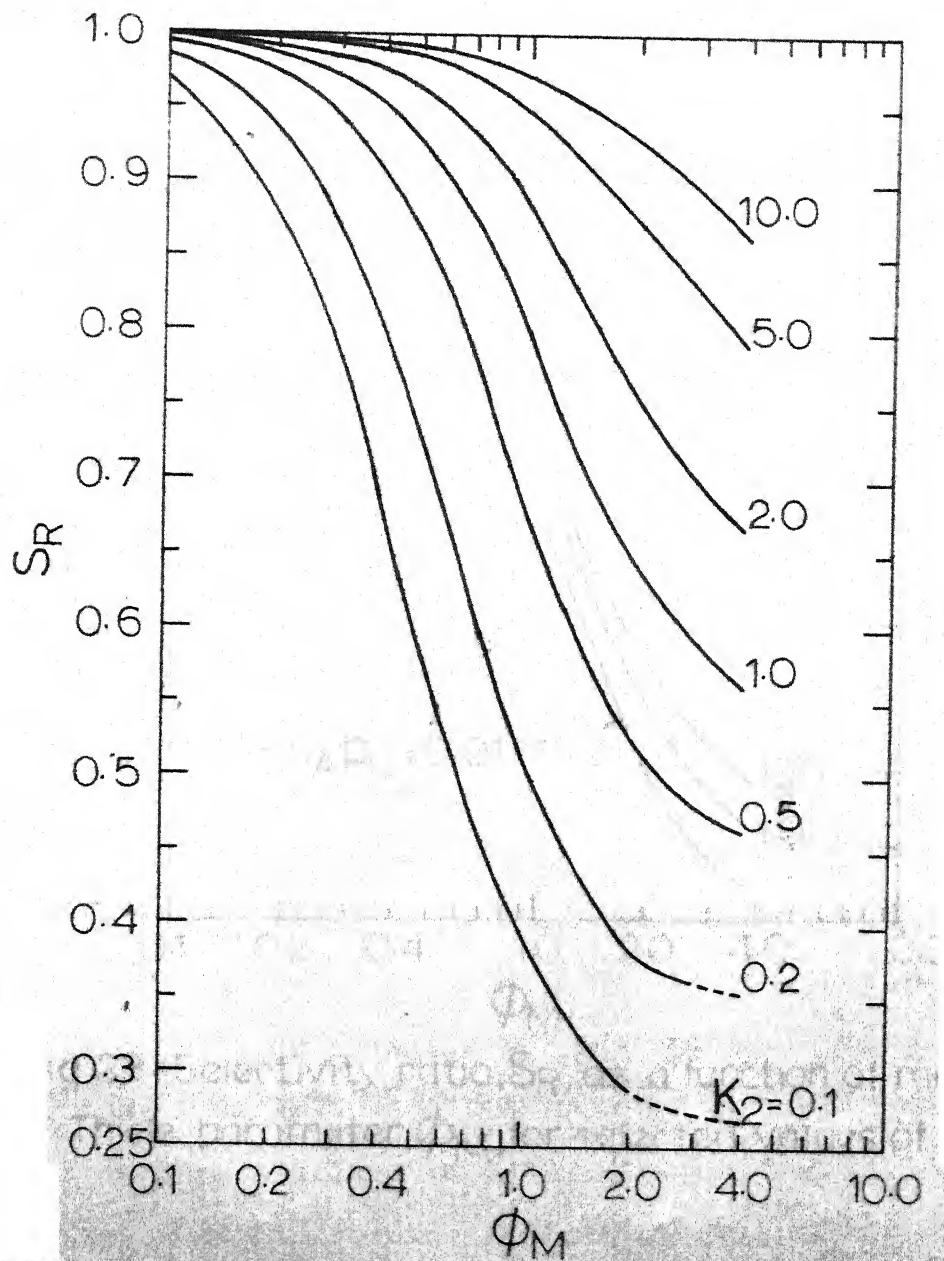
Fig. 22 - Selectivity ratio, S_R, as a function of modified Thiele parameter, Φ_M, for selected values of K_2.
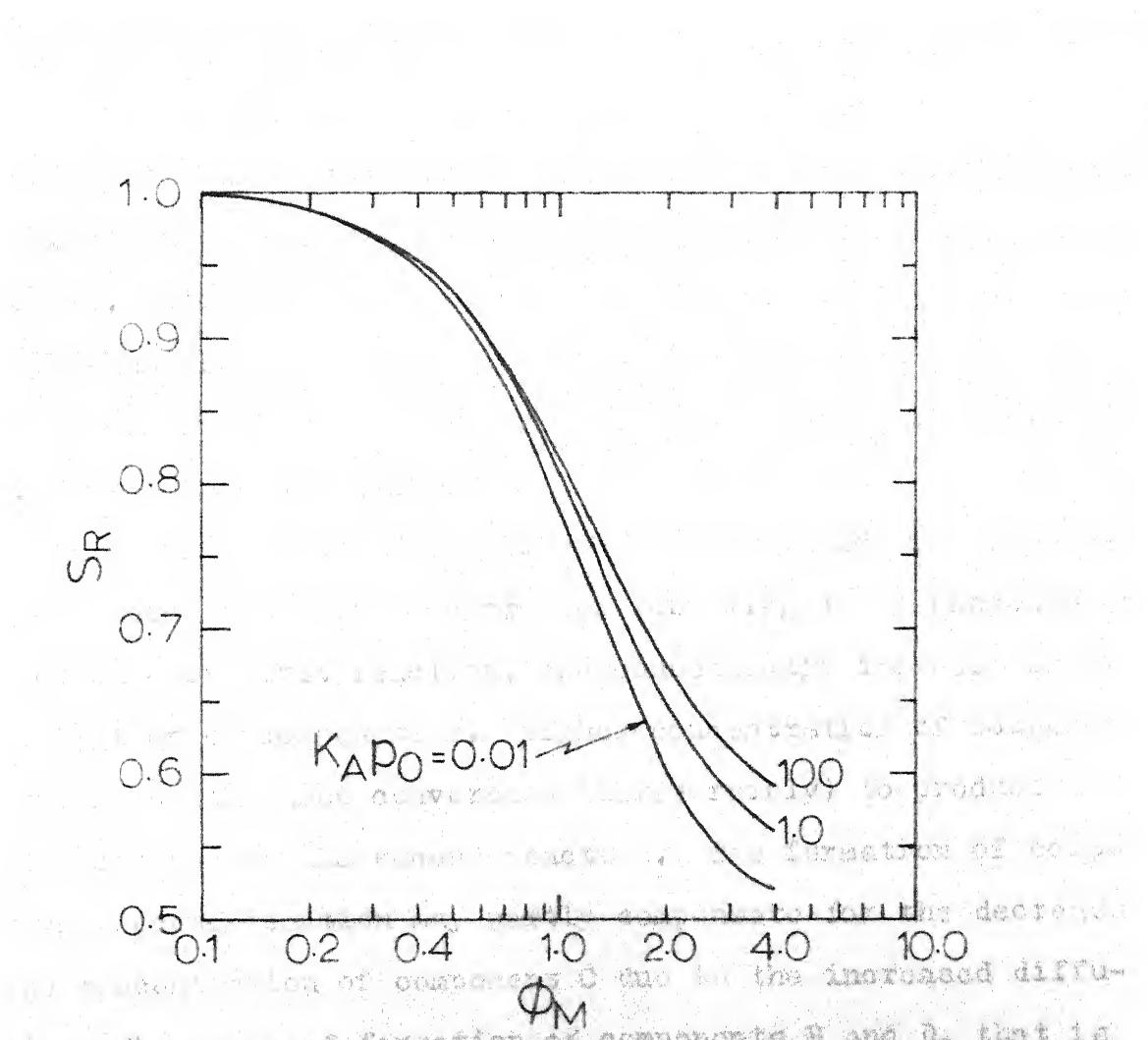
Fig. 23 - Selectivity ratio, S_R, as a function of modified Thiele parameter, Φ_M, for selected values of $K_A p_0$.

Diffusivity of component B is most important in series reactions. If diffusivity of B is large, component B will diffuse out of the pore at a faster rate and therefore, its concentration inside the pore will decrease. This will increase the formation of B while reaction of B to product D will decrease therefore, increase in the value of D_B/D_A, for given value of ϕ_M, will increase selectivity ratio quite significantly. Conversely the decrease in the value of D_B/D_A will decrease S_R significantly [Fig. 24 and Appendix A-24].

When diffusivity of component C is increased, its concentration inside the pore is decreased resulting in an increase in the net rate of first reaction, and consequently increase in the concentration of component B. Higher concentration of component B results in increased conversion (irreversibly) to produce D and C according to the second reaction. The formation of component C as per second reaction may partly compensate for the decrease in the concentration of component C due to the increased diffusivity. The rates of formation of components B and D, that is r_B and r_D are increased in absolute terms but their ratio r_B/r_D is decreased with increase in D_C/D_A at any given value of ϕ_M. The net result is, therefore, to decrease the selectivity ratio with increase in the diffusivity of component C [Fig.25 and Appendix A-25].
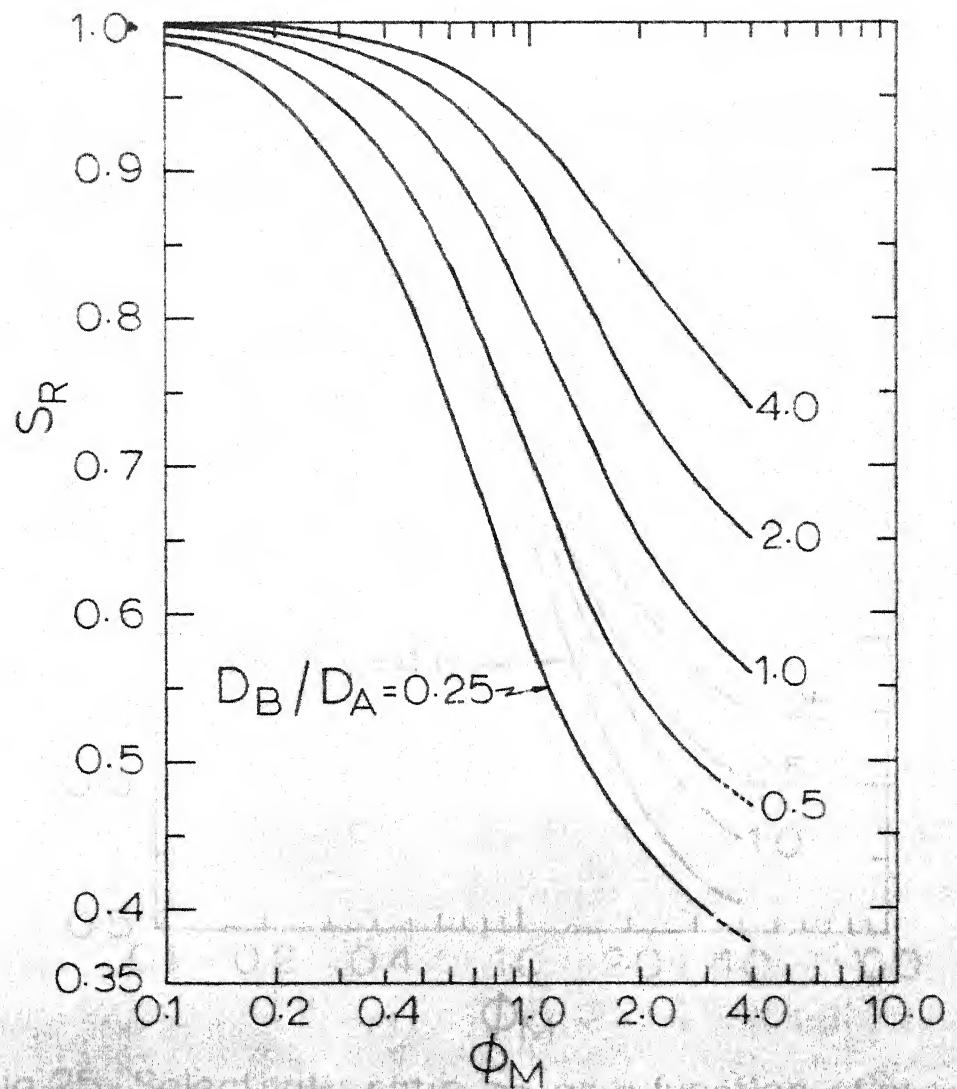
Fig.24 -Selectivity ratio, S_R, as a function of modified Thiele parameter, Φ_M, for selected values of D_B/D_A.
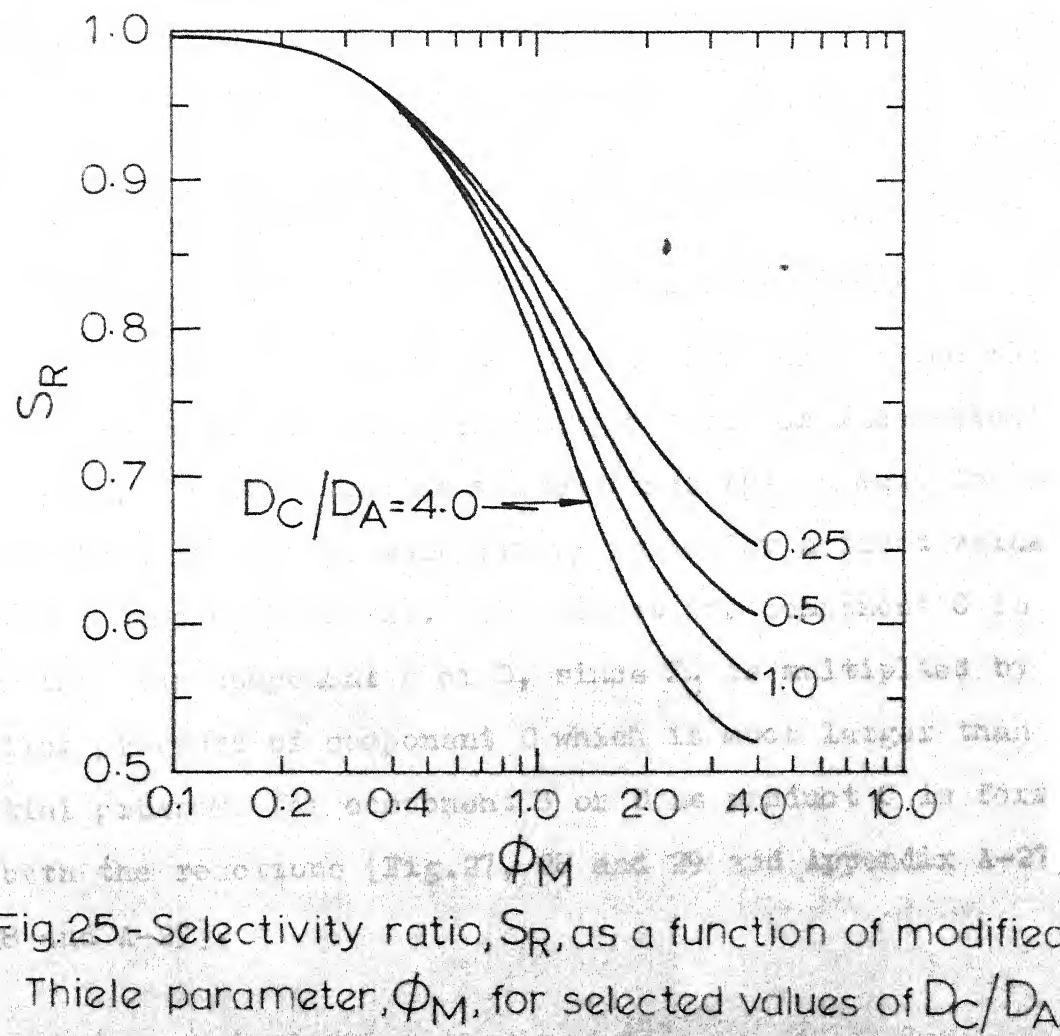
Fig.25 – Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_C/D_A.

The effect of change in the value of diffusivity of component D is similar to that for independent and parallel reactions, and is small in comparison to components B and C. Increase in the diffusivity of product D decreases its partial pressure and this decreases the value of denominator of the rate expressions and therefore decreases the reaction rate for both the reactions. The effect of diffusion is thus increased, which reduces the selectivity ratio as the diffusivity of product D is increased [Fig. 26 and Appendix A-26].

The effect of varying the adsorption equilibrium constant for component B, C or D is similar to that for independent reactions. Increase in the value of adsorption equilibrium constant increases the selectivity ratio for a fixed value of modified Thiele parameter. The effect for component C is more than that for component B or D, since K_C is multiplied by the partial pressure of component C which is much larger than the partial pressure for component B or D as product C is formed by both the reactions [Fig.27, 28 and 29 and Appendix A-27, A-28 and A-29].
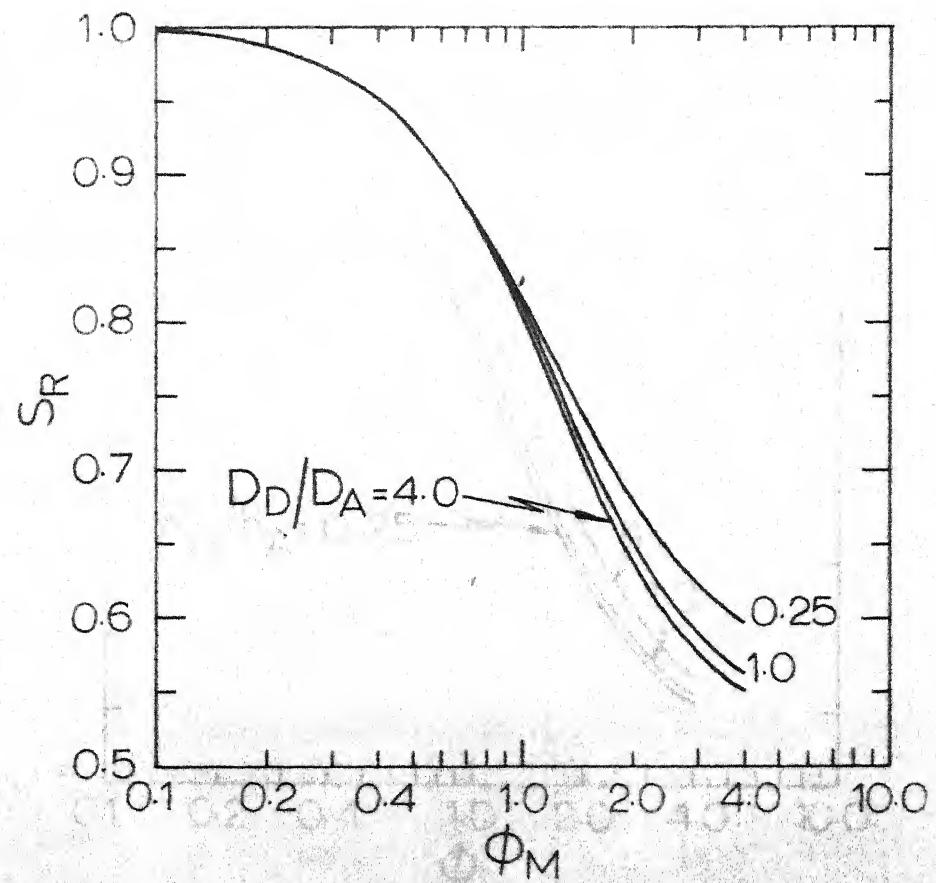
Fig. 26 – Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of D_D/D_A.
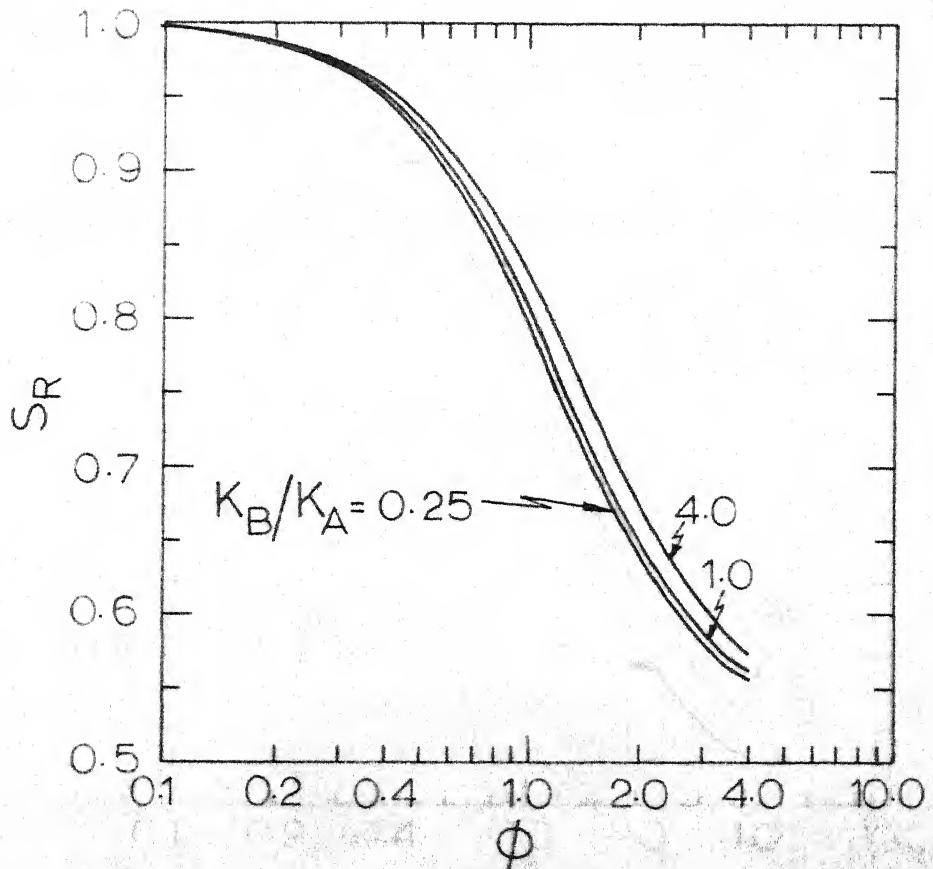
Fig.27-Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of K_B/K_A.
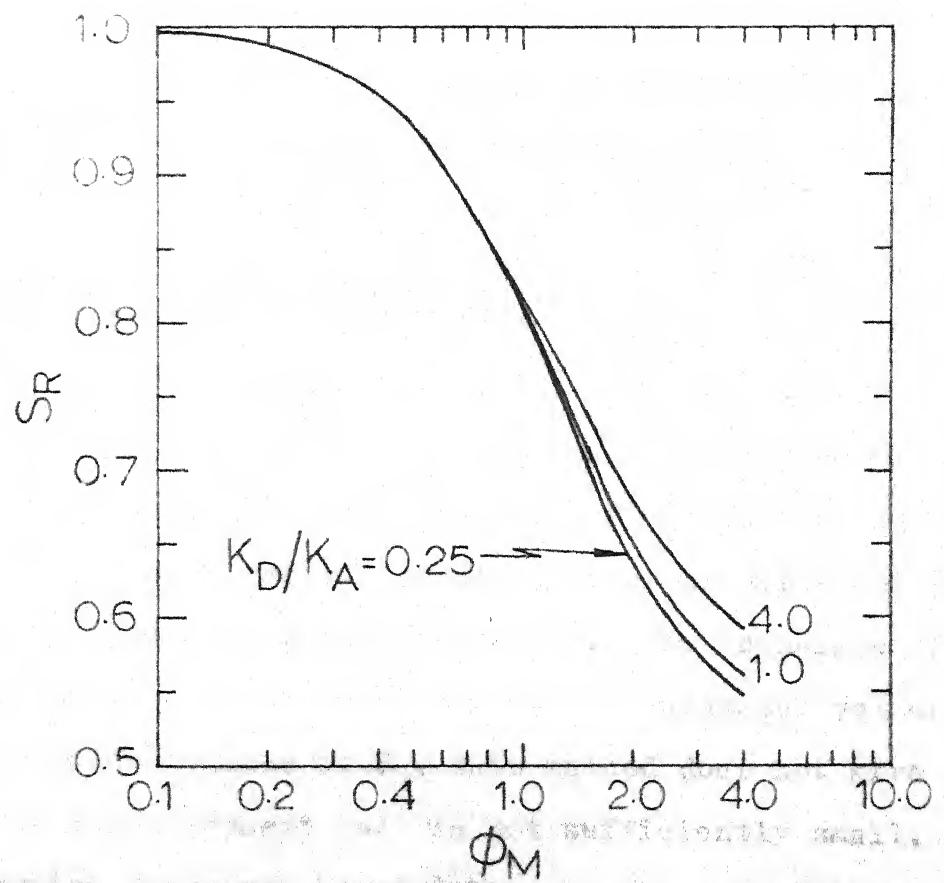
Fig. 29 - Selectivity ratio, S_R, as a function of modified Thiele parameter, ϕ_M, for selected values of K_D/K_A.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

A direct method to obtain the missing initial conditions of a system of nonlinear differential equations with two point boundary conditions using invariant imbedding concept is developed which involves less computational error and time. The only limitation of this new technique is its inability to use very small increments, say, less than 0.1. The technique is used to obtain the value of overall reaction rates of different products in a pore for complex reaction systems. The technique gives satisfactory results for modified Thiele parameter values upto two. For higher values of ϕ_M, this method does not give accurate results as the increment used is not sufficiently small. Quasi-linearization technique is used to solve these equations for values of ϕ_M upto a value of ten. However this technique has also failed in many cases, especially for series reactions, for ϕ_M values larger than three.

The selectivity of a complex reaction is significantly affected due to diffusion limitation in a catalyst pore. The magnitude depends upon the type of the reactions, reaction mechanism and the physical and chemical constants influencing the system. The effect of different variables investigated in

this work on the selectivity ratio is as follows:

    i. The selectivity ratio is found to decrease, except for two cases, with increase in modified Thiele parameter upto a value of five. Further increase in the value of $\emptyset_M$ does not effect the selectivity ratio. The selectivity ratio is found to increase with increase in $\emptyset_M$ only for independent reactions when the value of variable D_E/D_A or K_2 are less than unity.

    ii. For values of modified Thiele parameter less than 0.2, diffusion limitations are insignificant and selectivity ratio is close to unity.

    iii. The selectivity ratio is found to increase with increase in the value of K_1 for parallel as well as independent reactions. Contrary to this, selectivity ratio decreases with increase in the value of K_1 for series reactions. However the effect of change in K_1 is significant only for $\emptyset_M$ values greater than unity. The effect of thousand fold increase in the value of K_1 has maximum effect for the independent reactions and minimum for series reactions. In case of independent reactions, for K_1 value of 100, that is, first reaction is also essentially irreversible, the value of selectivity ratio remains close to unity even for $\emptyset_M$ values as large as ten.

iv.   When the second reaction is faster than the first, that is, values of K_2 less than unity, the selectivity ratio for independent reactions is always greater than unity and is found to increase with the increase in the value of $\emptyset_M$ or decrease in the value of K_2. For the value of K_2 greater than unity, selectivity ratio rapidly decreases with increase in the value of K_2 or $\emptyset_M$. In case of parallel and series reactions, lower values of selectivity ratio are obtained as the value of K_2 decreases from 10. to 0.1 and $\emptyset_M$ value increases.

v.   Increase in the value of $K_A p_o$ decreases the effect due to diffusion for all types of reactions studied, but the effect in each case is quite small for a given value of $\emptyset_M$. For very small value of $K_A p_o$ and for the range of K_i/K_A values investigated, the rate expressions becomes simple first or second order and $\emptyset_M$ values are close to ordinary Thiele parameter, $\emptyset$.

vi.   The effect of increase in the value of diffusivity ratio D_B/D_A is significant for all the three reaction schemes. The selectivity ratio increases with increase in the value of D_B/D_A. The maximum effect is observed for series reactions while the effect for parallel reactions is the least for all values of $\emptyset_M$ exceeding 0.5.

vii. The effect of increasing the diffusivity ratio D_C/D_A is to increase the selectivity ratio for independent and parallel reactions but to decrease it for series reactions. For values of $\emptyset_M$ less than unity, parallel reactions have largest effect followed by independent and then series reactions. However for large values of $\emptyset_M$, maximum effect is shown by independent reactions followed by series and then parallel reactions.

viii. The effect of increasing the diffusivity ratio D_D/D_A is comparatively insignificant for all the three reaction systems. Increase in the value of D_D/D_A decreases the selectivity ratio for independent and series reactions while its value is increased for parallel reactions. The effect increases with increase in the value of $\emptyset_M$ for the first two reaction systems, but in case of parallel reactions, maximum effect is observed at $\emptyset_M$ value close to unity.

ix. The effect of increase in the diffusivity ratio of the two reactants D_E/D_A in case of independent reaction is to decrease the selectivity ratio. The value of selectivity ratio is greater than unity, when the values of D_E/D_A are less than unity and it increases with increase in the value of $\emptyset_M$. The value of selectivity ratio is less than unity, when the values of D_E/D_A are larger than unity and it decreases with increase in $\emptyset_M$.

x. The effect of sixteenfold increase in the value of adsorption equilibrium constant ratio K_B/K_A does not have any significant effect on selectivity ratio. With increase in the value of K_B/K_A, the selectivity ratio is found to increase slightly for independent and series reactions with a maximum effect at $\emptyset_M$ value close to two. The selectivity ratio is found to decrease slightly for parallel reactions, with increase in the value of K_B/K_A with a maximum effect o at $\emptyset_M$ close to 0.7.

xi. The effect of varying the adsorption equilibrium constant ratios K_C/K_A and K_D/K_A is essentially similar to that of K_B/K_A but the magnitude of effect is comparatively more for K_C/K_A followed by K_D/K_A and then K_B/K_A.

xii. The effect of the change in the adsorption equil constant for component E in the case of independent reactions is somewhat peculiar. The selectivity ratio increases with increase in the value of K_E/K_A if the value of $\emptyset_M$ is less than two, but for values of $\emptyset_M$ larger than 2.3, S_R increases with decrease in the value of K_E/K_A. However the effect is small in magnitude.

B. Recommendations

The computed values of selectivity ratio are calculated by varying only one variable at a time while keeping the values of all other variables at unity. As such these curves may not be applicable to any actual system and it is therefore necessary, that a method is evolved to estimate the effect of diffusion on selectivity ratio when large number of variables have values other than unity. Once such a procedure is evolved, then any actual system can be handled using only limited data as presented in this thesis. A further extension of the work can also include the study of the effect on selectivity ratio of different concentrations of reactants and products at the pore mouth and then it will be possible to estimate the overall selectivity ratio for an integral reactor.

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APPENDICES

APPENDIX A-1

Selectivity Ratio, S_R, as a function of Modified
Thiele Parameter, $\emptyset_M$, for Various Values of K_1

Reaction $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
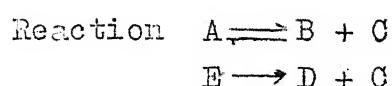
$\emptyset_M$ \ K_1 →	.1	.2	.5	1.	2.5	5.	10.	100.
.1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
.2	.998	.999	1.000	1.000	1.000	1.000	1.000	1.000
.4	.974	.986	.995	.997	.999	.999	1.000	1.000
.7	.862	.921	.965	.982	.991	.996	.998	1.000
1.	.731	.827	.915	.954	.976	.990	.995	1.000
2.	.555	.656	.785	.863	.920	.965	.982	.998
3.	.523	.621	.750	.834	.899	.953	.975	.997
4.	.518	.615	.742	.826	.892	.948	.972	.997
10.	.515	.612	.739	.823	.890	.947	.971	.997

APPENDIX A-2

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, $\emptyset_M$, for Various Values of K_2

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
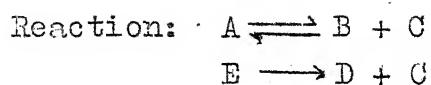
$K_2 \longrightarrow$ $\emptyset_M \downarrow$	.1	.2	.5	1.	2.	5.	10.
.1	1.029	1.013	1.003	1.000	.998	.997	.996
.2	1.109	1.050	1.012	1.000	.993	.989	.988
.4	1.357	1.170	1.043	.997	.974	.959	.954
.7	1.756	1.373	1.091	.982	.923	.886	.873
1.	2.047	1.530	1.122	.954	.859	.798	.776
2.	2.370	1.715	1.138	.863	.691	.568	.521
3.	2.403	1.735	1.136	.834	.629	.467	.402
4.	2.409	1.738	1.135	.826	.607	.424	.345
10.	2.423	1.743	1.136	.823	.597	.390	.284

APPENDIX A-3

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, $\emptyset_M$, for Various Values of $K_A p_0$

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
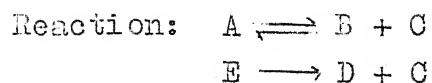
$K_A p_0 \rightarrow$ / $\emptyset_M \downarrow$	.01	.1	1.	10.	100.
.1	1.000	1.000	1.000	1.000	1.000
.2	1.000	1.000	1.000	1.000	1.000
.4	.997	.997	.997	.997	.997
.7	.980	.980	.982	.984	.984
1.	.946	.947	.954	.959	.960
2.	.846	.849	.863	.875	.877
3.	.822	.824	.834	.843	.845
4.	.816	.818	.826	.832	.834
10.	.815	.816	.823	.829	.830

APPENDIX A-4

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of D_B/D_A

Reaction: $A \rightleftharpoons B + C$
$E \longrightarrow D + C$
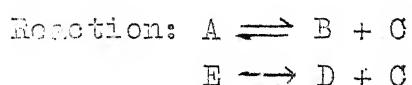
ϕ_M \ D_B/D_A →	.25	.50	1.	2.	4.
.1	1.000	1.000	1.000	1.000	1.000
.2	.999	1.000	1.000	1.000	1.000
.4	.990	.995	.997	.999	.999
.7	.944	.967	.982	.991	.995
1.	.872	.920	.954	.975	.987
2.	.708	.792	.863	.918	.954
3.	.665	.755	.834	.897	.941
4.	.655	.745	.826	.890	.936
10.	.652	.742	.823	.888	.935

APPENDIX A-5

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of D_C/D_A

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
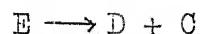
$D_C/D_A \rightarrow$ $\phi_M \downarrow$	.25	.50	1.	2.	4.
.1	.999	1.000	1.000	1.000	1.000
.2	.999	1.000	1.000	1.000	1.000
.4	.991	.995	.997	.999	.999
.7	.950	.969	.982	.990	.995
1.	.890	.925	.954	.974	.986
2.	.738	.802	.863	.914	.951
3.	.693	.763	.834	.895	.938
4.	.675	.751	.826	.888	.934
10.	.668	.748	.823	.887	.933

APPENDIX A-6

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of D_D/D_A

Reaction:
$A \rightleftharpoons B + C$
$E \longrightarrow D + C$
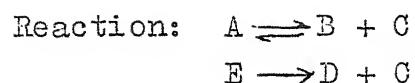
ϕ_M \ D_D/D_A $\rightarrow$	.25	.50	1.	2.	4.
.1	1.000	1.000	1.000	1.000	1.000
.2	1.000	1.000	1.000	1.000	1.000
.4	.997	.997	.997	.997	.997
.7	.985	.983	.982	.982	.981
1.	.962	.957	.954	.952	.951
2.	.885	.872	.863	.859	.856
3.	.852	.841	.834	.831	.829
4.	.839	.831	.826	.823	.821
10.	.834	.828	.823	.821	.820

APPENDIX A-7

Selectivity Ratio, S_R, as a Function of Modified Thiele Parameter, $\emptyset_M$, for Various Values of D_E/D_A

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
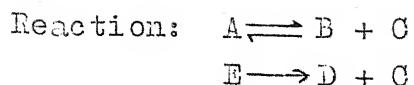
$\emptyset_M$ \ D_E/D_A	.25	.50	1.	2.	4.
.1	1.010	1.004	1.000	.998	.997
.2	1.039	1.013	1.000	.994	.990
.4	1.143	1.045	.997	.973	.962
.7	1.346	1.104	.982	.922	.892
1.	1.517	1.148	.954	.857	.809
2.	1.709	1.190	.863	.683	.593
3.	1.728	1.192	.834	.613	.497
4.	1.730	1.193	.826	.589	.454
10.	1.735	1.194	.823	.574	.412

APPENDIX A-8

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of K_B/K_A

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
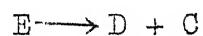
ϕ_M \ K_B/K_A →	.25	.5	1.	2.	4.
.1	1.000	1.000	1.000	1.000	1.000
.2	1.000	1.000	1.000	1.000	1.000
.4	.997	.997	.997	.997	.997
.7	.981	.982	.982	.983	.985
1.	.951	.952	.954	.957	.962
2.	.858	.860	.863	.870	.881
3.	.831	.832	.834	.839	.847
4.	.823	.824	.826	.829	.835
10.	.821	.822	.823	.826	.831

APPENDIX A-9

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of K_C/K_A

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
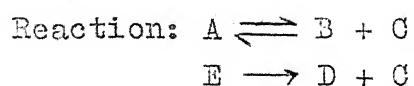
K_C/K_A $\longrightarrow$ ϕ_M $\downarrow$	0.0	.25	.50	1.	2.	4.
.1	1.000	1.000	1.000	1.000	1.000	1.000
.2	1.000	1.000	1.000	1.000	1.000	1.000
.4	.997	.997	.997	.997	.997	.998
.7	.980	.980	.981	.982	.984	.987
1.	.945	.948	.950	.954	.960	.968
2.	.846	.851	.855	.863	.877	.898
3.	.822	.825	.828	.834	.845	.861
4.	.816	.819	.821	.826	.834	.847
10.	.815	.817	.819	.823	.830	.839

APPENDIX A-10

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of K_D/K_A

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
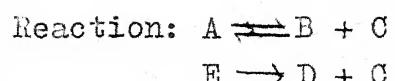
ϕ_M $\diagdown$ $K_D/K_A \longrightarrow$	0.0	.25	.50	1.	2.	4.
.1	1.000	1.000	1.000	1.000	1.000	1.000
.2	1.000	1.000	1.000	1.000	1.000	1.000
.4	.997	.997	.997	.997	.997	.997
.7	.981	.981	.982	.982	.983	.985
1.	.950	.951	.952	.954	.957	.962
2.	.854	.856	.859	.863	.872	.885
3.	.827	.829	.831	.834	.841	.852
4.	.820	.822	.823	.826	.831	.839
10.	.818	.820	.821	.823	.828	.834

APPENDIX A-11

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of K_E/K_A

Reaction: $A \rightleftharpoons B + C$

$E \longrightarrow D + C$
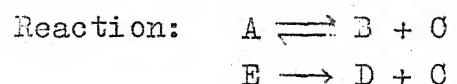
ϕ_M \ K_E/K_A	.25	.50	1.	2.	4.
.1	1.000	1.000	1.000	1.000	1.000
.2	1.000	1.000	1.000	1.000	1.000
.4	.996	.997	.997	.998	.999
.7	.978	.979	.982	.986	.992
1.	.948	.950	.954	.961	.973
2.	.864	.863	.863	.865	.872
3.	.839	.837	.834	.831	.829
4.	.831	.829	.826	.821	.813
10.	.829	.827	.823	.818	.809

APPENDIX A-12

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of K_1

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
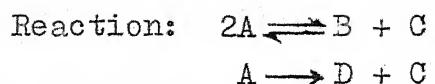
ϕ_M \ K_1	.1	.2	.5	1.	2.	5.	10.	100.
.1	.996	.996	.996	.996	.996	.996	.996	.996
.2	.983	.984	.984	.984	.984	.984	.984	.984
.4	.936	.940	.943	.944	.944	.945	.945	.945
.7	.824	.847	.861	.866	.869	.870	.871	.871
1.	.706	.748	.779	.791	.798	.802	.803	.804
2.	.496	.543	.599	.631	.651	.665	.669	.674
3.	.452	.488	.535	.566	.592	.613	.622	.629
4.	.443	.476	.516	.544	.569	.593	.605	.617
10.	.438	.470	.506	.529	–	–	–	–

APPENDIX A-14

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of $K_A p_o$

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
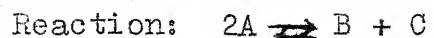
$K_A p_o \rightarrow$ $\phi_M \downarrow$	.01	.1	1.	10.	100.
.1	.997	.996	.996	.996	.996
.2	.987	.986	.984	.984	.984
.4	.950	.948	.944	.944	.945
.7	.867	.864	.866	.874	.876
1.	.775	.775	.791	.811	.815
2.	.573	.578	.631	.676	.684
3.	.513	.512	.566	.619	.627
4.	.498	.491	.544	.596	.605
10.	.484	–	.529	.581	.589

APPENDIX A-13

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of K_2

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
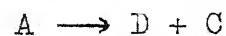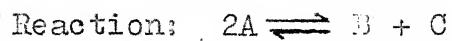
ϕ_M \ $K_2 \rightarrow$	.1	.2	.5	1.	2.	5.	10.
.1	.956	.978	.991	.996	.998	.999	1.000
.2	.857	.920	.967	.984	.993	.997	.997
.4	.670	.778	.892	.944	.972	.989	.995
.7	.533	.622	.770	.866	.929	.972	.986
1.	.482	.539	.676	.791	.882	.950	.975
2.	.456	.472	.534	.631	.752	.879	.936
3.	.449	.461	.502	.566	.671	.819	.898
4.	.446	.457	.492	.544	.629	.772	.866
10.	.438	.451	.483	.529	.594	.697	.777

APPENDIX A-15

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of D_B/D_A

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
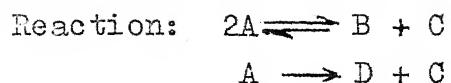
ϕ_M \ D_B/D_A	.25	.50	1.	2.	4.
.1	.995	.996	.996	.996	.996
.2	.980	.983	.984	.985	.985
.4	.931	.939	.944	.946	.947
.7	.840	.857	.866	.871	.874
1.	.752	.776	.791	.800	.805
2.	.559	.601	.631	.652	.664
3.	.495	.533	.566	.597	.614
4.	.481	.514	.544	.570	−
10.	.473	.504	.529	−	−

APPENDIX A-16

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, $\emptyset_M$, for Various Values of D_C/D_A

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
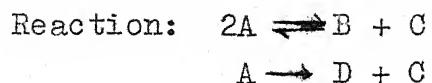
$\emptyset_M$ $\downarrow$ \ D_C/D_A $\rightarrow$	.25	.50	1.	2.	4.
.1	.992	.995	.996	.997	.997
.2	.972	.980	.984	.986	.988
.4	.910	.931	.944	.951	.954
.7	.813	.845	.866	.879	.886
1.	.731	.766	.791	.808	.818
2.	.572	.604	.631	.657	.673
3.	.508	.538	.566	.595	—
4.	.484	.514	.544	—	.599
10.	.464	.499	.529	—	—

APPENDIX A-17

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of D_D/D_A

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
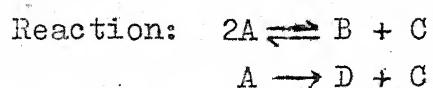
ϕ_M \ D_D/D_A →	.25	.50	1.	2.	4.
.1	.994	.995	.996	.996	.997
.2	.976	.981	.984	.986	.986
.4	.920	.935	.944	.948	.951
.7	.830	.853	.866	.873	.877
1.	.755	.778	.791	.798	.802
2.	.613	.626	.631	.631	.633
3.	.555	.567	.566	.567	.564
4.	.531	.542	.544	.545	.543
10.	.503	.522	.529	–	–

APPENDIX A-18

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of K_B/K_A

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
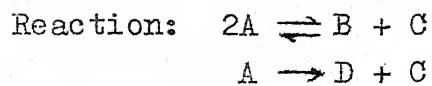
ϕ_M \ $K_B/K_A \rightarrow$	.25	.50	1.	2.	4.
.1	.996	.996	.996	.996	.995
.2	.985	.985	.984	.983	.980
.4	.947	.946	.944	.940	.933
.7	.870	.869	.866	.861	.852
1.	.795	.793	.791	.787	.780
2.	.632	.632	.631	.631	.627
3.	.568	.567	.566	.564	.562
4.	.546	.546	.544	.542	.539
10.	.531	.530	.529	.527	.522

APPENDIX A-19

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, $\emptyset_M$, for Various Values of K_C/K_A

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
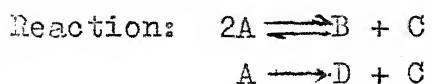
$K_C/K_A \rightarrow$ $\emptyset_M \downarrow$	0.0	.25	.50	1.	2.	4.
.1	.997	.997	.997	.996	.995	.992
.2	.989	.987	.986	.984	.980	.972
.4	.957	.954	.950	.944	.932	.912
.7	.887	.882	.876	.866	.849	.821
1.	.811	.806	.801	.791	.775	.747
2.	.629	.631	.632	.631	.623	.608
3.	.562	.564	.565	.566	.565	.554
4.	–	–	.546	.544	.542	.526
10.	–	–	–	.529	.519	.498

APPENDIX A-20

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of K_D/K_A

Reaction: $2A \rightleftharpoons B + C$

$A \longrightarrow D + C$
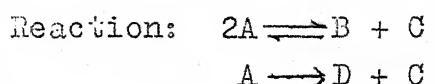
ϕ_M \ $K_D/K_A \longrightarrow$	0.0	.25	.50	1.	2.	4.
.1	.997	.997	.996	.996	.995	.994
.2	.987	.986	.986	.984	.981	.976
.4	.953	.951	.948	.944	.935	.920
.7	.881	.877	.873	.866	.853	.830
1.	.806	.802	.798	.791	.778	.755
2.	.629	.630	.631	.631	.630	.618
3.	.562	.563	.564	.566	.567	.557
4.	–	.544	.544	.544	.542	.533
10.	–	–	–	.529	.521	.504

APPENDIX A-21

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of K_1

Reaction: $A \rightleftharpoons B + C$

$B \longrightarrow D + C$

ϕ_M \ $K_1 \rightarrow$	.1	.2	.5	1.	2.	5.	10.	100.
.1	.997	.997	.997	.997	.997	.997	.997	.997
.2	.987	.987	.987	.987	.987	.987	.987	.987
.4	.952	.952	.952	.952	.952	.952	.952	.952
.7	.882	.880	.879	.879	.878	.878	.878	.878
1.	.816	.810	.806	.804	.803	.802	.802	.802
2.	.692	.675	.655	.646	.640	.636	.635	.635
3.	.64	.624	.600	.588	.580	.573	.570	.570
4.	—	.60	—	.563	—	—	—	—
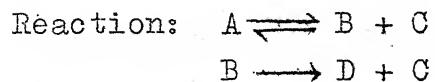
APPENDIX A-22

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of K_2

Reaction: $A \rightleftharpoons B + C$

$B \longrightarrow D + C$
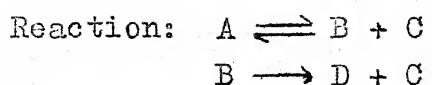
ϕ_M \ $K_2 \rightarrow$	.1	.2	.5	1.	2.	5.	10.
.1	.968	.984	.993	.997	.998	.999	1.000
.2	.886	.939	.975	.987	.994	.997	.999
.4	.687	.806	.910	.952	.975	.990	.995
.7	.484	.624	.790	.879	.934	.972	.986
1.	.388	.511	.688	.804	.887	.950	.974
2.	.29	.381	.526	.646	.760	.875	.930
3.	–	–	–	.588	.696	.823	.893
4.	..	–	–	–	.667	.791	.867

APPENDIX A-23

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, $\emptyset_M$, for Various Values of $K_A p_o$

Reaction: $A \rightleftharpoons B + C$

$B \longrightarrow D + C$
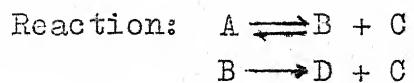
$K_A p_o \rightarrow$ $\emptyset_M \downarrow$	.01	.1	1.	10.	100.
.1	.997	.997	.997	.997	.997
.2	.987	.987	.987	.987	.987
.4	.950	.951	.952	.953	.954
.7	.869	.871	.879	.885	.886
1.	.781	.785	.804	.817	.820
2.	.600	.609	.646	.670	.674
3.	–	–	.588	.613	.618
4.	–	–	–	.59	.59

APPENDIX A-24

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of D_B/D_A

Reaction: $A \rightleftharpoons B + C$

$B \longrightarrow D + C$
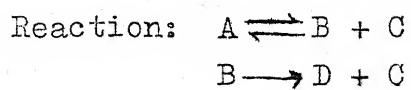
ϕ_M \ D_B/D_A $\rightarrow$	.25	.50	1.	2.	4.
.1	.987	.993	.997	.998	.999
.2	.952	.975	.987	.993	.997
.4	.847	.912	.952	.975	.987
.7	.692	.798	.879	.932	.963
1.	.584	.701	.804	.881	.933
2.	.443	.541	.646	.747	.834
3.	—	.495	.588	.683	.773
4.	—	—	—	.654	.740

APPENDIX A-25

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, ϕ_M, for Various Values of D_C/D_A

Reaction: $A \rightleftharpoons B + C$
$B \longrightarrow D + C$
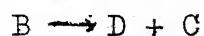
ϕ_M \ D_C/D_A	.25	.5	1.	2.	4.
.1	.997	.997	.997	.997	.997
.2	.987	.987	.987	.987	.987
.4	.956	.954	.952	.951	.951
.7	.898	.887	.879	.874	.871
1.	.843	.831	.804	.792	.784
2.	.727	.684	.646	.617	.598
3.	.677	.628	.588	.558	−
4.	.653	.605	−	−	−

APPENDIX A-26

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, $\emptyset_M$, for Various Values of D_D/D_A

Reaction: $A \rightleftharpoons B + C$

$B \longrightarrow D + C$
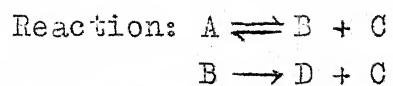
$\emptyset_M$ \ $D_D/D_A \rightarrow$	.25	.50	1.	2.	4.
.1	.997	.997	.997	.997	.997
.2	.987	.987	.987	.987	.987
.4	.952	.952	.952	.952	.952
.7	.882	.880	.879	.878	.878
1.	.814	.808	.804	.802	.801
2.	.677	.658	.646	.639	.635
3.	.623	.602	.588	.580	.576
4.	.598	—	—	—	—

APPENDIX A-28

Selectivity Ratio, S_R, as a Function of Modified
Thiele Parameter, $\emptyset_M$, for Various Values of K_C/K_A

Reaction: $A \rightleftharpoons B + C$

$B \longrightarrow D + C$
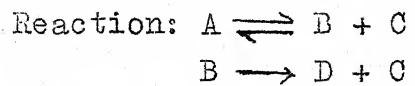
K_C/K_A $\longrightarrow$ $\emptyset_M \downarrow$	0.0	.25	.50	1.0	2.	4.
.1	.997	.997	.997	.997	.997	.997
.2	.987	.987	.987	.987	.987	.987
.4	.950	.951	.951	.952	.954	.956
.7	.869	.871	.874	.879	.886	.897
1.	.780	.787	.793	.804	.820	.842
2.	.599	.613	.625	.646	.677	.718
3.	~	~	~	.588	.618	.660
4.	~	~	~	~	.593	.630

APPENDIX A-29

Selectivity Ratio, S_R, as a Function of Modified

Thiele Parameter, ϕ_M, for Various Values of K_D/K_A

Reaction: $A \rightleftharpoons B + C$
$B \longrightarrow D + C$
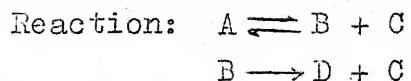
$K_D/K_A \rightarrow$ $\phi_M \downarrow$	0.0	.25	.50	1.	2.	4.
.1	.997	.997	.997	.997	.997	.997
.2	.987	.987	.987	.987	.987	.987
.4	.952	.952	.952	.952	.952	.952
.7	.877	.878	.873	.879	.880	.882
1.	.800	.801	.802	.804	.808	.814
2.	.631	.635	.639	.646	.658	.677
3.	—	.58	.58	.588	.601	.623
4.	—	—	—	—	—	.600

APPENDIX B-1

COMPUTER PROGRAMME FOR INVARIANT IMBEDDING TECHNIQUE

```
$ JOB      CGF041,TIME008,NAME A B LAL   PAR REAC K1 K2 KAPO
$IBJOB
$IBFTC
      DIMENSION U(4,4),V(4,4),W(4,4),X(3),AA(2),BB(2),CC(2)
      READ 61,((U(K,L),L=1,3),K=1,3)
   61 FORMAT(3F15.8)
      C0=0.
      D0=0.
      COMMON A,B1,B2,B3
      MM=0
    2 READ 51,A,B1,B2,B3
   51 FORMAT(4F7.2)
      M=0
      DO 99 J=8,10
      N=0
      N1=0
      N2=0
      N3=0
      N4=0
      N5=0
      R=J
      Q=1./R
      P=Q*Q
      C=C0
      D=D0
    5 N=N+1
      C1=C-P*F(C,D)
      D1=D-P*G(C,D)
      C2=C1-P*F(C1,D1)
      D2=D1-P*G(C1,D1)
      C1=C2-P*F(C2,D2)
      D1=D2-P*G(C2,D2)
      GO TO(7,28,7,29,7,1,7,12,7,3,7,3,7,1,7,14,7,6,7,6,7,1,7,6,7,3,7,3,
     1 7,1,7,21,7,8,7,8,7,1,7,8,7,3,7,3,7,1,7,8,7,6,7,6,7,1,7,6,7,3,7,3,
     2 7,1,7,19,7,4,7,4,7,1,7,4,7,3,7,3,7,1,7,4,7,6,7,6,7,1,7,6,7,3,7,3,
     3 7,1,7,4,7,8,7,8,7,1,7,8,7,3,7,3,7,1,7,8,7,6,7,6,7,1,7,6,7,3,7,3,
     4 7,1,7,25),N
    7 C3=C-P*(F(C,D)+F(C1,D1)+F(C2,D2))
      D3=D-P*(G(C,D)+G(C1,D1)+G(C2,D2))
      C=C3
      D=D3
      GO TO 5
```

```
28    C=C0
      D=D0
11    C4=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3))
      D4=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3))
      C=C4
      D=D4
      GO TO 5
29    C=C0
      D=D0
15    C5=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4))
      D5=D-P*(G(C,D) G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4))
1     C=C5
      D=D5
      N1=N1+1
      GO TO(5,11,5,11,5,11,5,11,5,11,5,11,5,11,5,11,
     1      5,11,5,11,5,11,5,11,5,11,5,11,5,11,5,11),N1
12    C=C0
      D=D0
20    C6=C-P*(F(C,D) F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5))
      D6=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5))
3     C=C6
      D=D6
      N2=N2+1
      GO TO(5,11,15,5,11,15,5,11,15,5,11,15,
     1      5,11,15,5,11,15,5,11,15,5,11,15),N2
14    C=C0
      D=D0
18    C7=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
     1 F(C6,D6))
      D7=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
     1 G(C6,D6))
6     C=C7
      D=D7
      N3=N3+1
      GO TO(5,11,15,20,5,11,15,20,5,11,15,20,5,11,15,20),N3
21    C=C0
      D=D0
22    C8=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
     1 F(C6,D6)+F(C7,D7))
      D8=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
     1 G(C6,D6)+G(C7,D7))
      IF(J-8)8,40,8
40    V(1,4)=(C8-C0)/Q
      W(1,4)=(D8-D0)/Q
      GO TO 99
8     C=C8
      D=D8
      N4=N4+1
      GO TO(5,11,15,20,18,5,11,15,20,18),N4
```

```
19   C=C0
     D=D0
     C9=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
    1 F(C6,D6)+F(C7,D7)+F(C8,D8))
     D9=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
    1 G(C6,D6)+G(C7,D7)+G(C8,D8))
     IF(J-9)4,41,4
41   V(2,4)=(C9-C0)/Q
     W(2,4)=(D9-D0)/Q
     GO TO 99
4    C=C9
     D=D9
     N5=N5+1
     GO TO(5,11,15,20,18,22),N5
25   C10=C0-P*(F(C0,D0)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
    1 F(C6,D6)+F(C7,D7)+F(C8,D8)+F(C9,D9))
     D10=D0-P*(G(C0,D0)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
    1 G(C6,D6)+G(C7,D7)+G(C8,D8)+G(C9,D9))
     V(3,4)=(C10-C0)/Q
     W(3,4)=(D10-D0)/Q
99   CONTINUE
68   DO 62 K=1,3
     DO 62 L=1,3
62   V(K,L)=U(K,L)
     DO 63 I=1,2
     II=I+1
     DO 63 K=II,3
     DO 63 L=II,4
63   V(K,L)=V(K,L)-V(I,L)*V(K,I)/V(I,I)
     DO 64 LQ=3,4
     LL=6-LQ
     LJ=LL-1
     DO 64 K=1,LJ
64   V(K,4)=V(K,4)-V(LL,4)*V(K,LL)/V(LL,LL)
     DO 65 K=1,3
65   X(K)=V(K,4)/V(K,K)
     DO 67 K=1,3
67   V(K,4)=W(K,4)
     M=M+1
     AA(M)=X(1)
     BB(M)=X(2)
     CC(M)=X(3)
     IF(M-2)68,98,98
98   AB=AA(1)*(1.+B3*(1.+2.*B2))/((2.*AA(1)+AA(2))*B2*B3)
     PRINT 69,A,B1,B2,B3,    AB,AA(1),AA(2),BB(1),CC(1),BB(2),CC(2)
69   FORMAT(4F7.2,F14.4,F16.6,F11.6,4F10.4)
     MM=MM+1
     IF(MM-200) 2,97,97
97   STOP
     END
```

```
$IBFTC FUN1
       FUNCTION F(C,D)
       COMMON A,B1,B2,B3
       F=-A*A*B3/(1.+B3)*((1.-2.*C-D)**2-C*(C+D)/B1)/(1.+B3*D/(1.+B3))**2
       RETURN
       END
$IBFTC FUN2
       FUNCTION G(C,D)
       COMMON A,B1,B2,B3
       G=-A*A/B2*(1.-2.*C-D)/(1.+B3*D/(1.+B3))
       RETURN
       END
$ENTRY
       1.                    .125            .015625
       1.                    .11111111       .01234568
       1.                    .1              .01
```

APPENDIX B-2

COMPUTER PROGRAMME FOR QUASILINEARIZATION TECHNIQUE

```
$JOB      CGF041,TIME008,NAME A B LAL   IND REAC K1 K2 KAPO
$IBJOB
$IBFTC
       DIMENSION X(1000),Y(1000),H(1000),E(1000),P(1000),Q(1000),G(1000),
      1 PP(1000),QQ(1000),GG(1000),R(1000),S(1000),V(1000),W(1000)
       NN=0
       B=.1E+07
   11  READ 1,A,B1,B2,B3
   1   FORMAT(4F7.2)
       XO=0.
       YO=0.
       B5=B3/(1.+2.*B3)
       DO 2 I=1,1000
       X(I)=0.001
   2   Y(I)=0.001
   7   DO 3 I=1,999
       R(I)=X(I)-(.5-X(I))*(1.-X(I)-Y(I))/B1
       S(I)=1.-B5*(X(I)+Y(I))
       H(I)=-(2.*B+A*A*(R(I)*B5/S(I)**2+(1.+(1.5-2.*X(I)-Y(I))/B1)/S(I)))
       E(I)=-(2.*B+A*A/B2*(B5*Y(I)/S(I)**2+1./S(I)))
       V(I)=A*A*(R(I)/S(I)-X(I)*(R(I)*B5/S(I)**2+(1.+(1.5-2.*X(I)-Y(I))
      1  /B1)/S(I)))
   3   W(I)=A*A/B2*(Y(I)/S(I)-Y(I)*(B5*Y(I)/S(I)**2+1./S(I)))
       W(1)=W(1)-.5*B
       V(1)=V(1)-.5*B
       H(999)=H(999)+B
       E(999)=E(999)+B
       P(1)=H(1)
       Q(1)=B/P(1)
       G(1)=V(1)/P(1)
       PP(1)=E(1)
       QQ(1)=B/PP(1)
       GG(1)=W(1)/PP(1)
       DO 4 I=2,999
       P(I)=H(I)-B*Q(I-1)
       Q(I)=B/P(I)
       G(I)=(V(I)-B*G(I-1))/P(I)
       PP(I)=E(I)-B*QQ(I-1)
       QQ(I)=B/PP(I)
   4   GG(I)=(W(I)-B*GG(I-1))/PP(I)
       X(999)=G(999)
       Y(999)=GG(999)
```

```
      DO 5 I=1,998
      M=999-I
      X(M)=G(M)-Q(M)*X(M+1)
5     Y(M)=GG(M)-QQ(M)*Y(M+1)
      X1=(X(1)-.5)*1000.
      Y1=(Y(1)-.5)*1000.
      IF(ABS(XO-X1)-.001) 15,15,16
15    IF(ABS(YO-Y1)-.001) 17,17,16
16    XO=X1
      YO=Y1
      GO TO 7
17    AB=X1/(Y1*B2)
      PRINT6,A,B1,B2,B3,   AB,X1,Y1
6     FORMAT(4F7.2,3F15.5)
8     NN=NN+1
      IF(NN-99)11,88,88
88    STOP
      END
$ENTRY
```

APPENDIX C

ILLUSTRATIVE EXAMPLE: DEHYDRATION OF ETHANOL

Butt et.al [39] considered the dehydration of ethyl
alcohol on alumina catalyst and obtained the following rate
expressions at $274^{\circ}C$ in gram moles per min. per gram of catalyst.

$$r_B = \frac{0.00627 \times 0.00135\ p_A^2}{4. \times (1+0.00135\ p_A + 0.001\ p_B + 0.00151\ p_C)^2} \tag{1a}$$

$$r_D = \frac{0.000099 \times 0.00135\ p_A}{(1+0.00135\ p_A + 0.001\ p_B + 0.00151\ p_C)} \tag{1b}$$

where the reactions can be expressed as

$$2A \rightleftharpoons B + C$$
$$A \longrightarrow D + C$$

Component A stands for ethyl alcohol, B for diethyl ether, C for
water and D for ethylene. The partial pressures in the above rate
expressions are in mm. of Hg. The density of alumina catalyst
pallet is 0.80 gram/cc and porosity is 0.667. Changing the
partial pressure in atmosphere and rate of reactions in gram
mole per sec. per cc of pore volume, the following rate expressions
are obtained:

$$r_B = \frac{0.000033\ p_A^2}{(1 + 1.026\ p_A + 0.76\ p_B + 1.1576\ p_C)^2} \tag{2a}$$

$$r_D = \frac{0.00000203 \, p_A}{(1 + 1.026 \, p_A + 0.76 \, p_B + 1.1576 \, p_C)^2} \qquad (2b)$$

Here

$$K_A = 1.026$$

$$K_B = 0.76$$

$$K_C = 1.157$$

$$K_D = 0.0$$

$$D_A^* = 0.101$$

$$D_B^* = 0.0736$$

$$D_C^* = 0.216$$

$$D_D^* = 0.139$$

Therefore $K_A p_o = 1.026$

$$k_1 K_A = .000033/1.026 = .0000322$$

$$K_1 = \infty$$

$$K_2 = k_1 K_A / k_2 K_A = k_1/k_2 = \frac{0.0000322}{0.00000203} = 15.86$$

$$1 + K_A p_o = 2.026$$

In this problem, since the values of all the variables are different than unity, the figures given earlier cannot be used directly and the problem has to be solved by Computer. Equations 25a and 25b of Chapter II can be written as

---

*The values for effective diffusion coefficients are taken as one-half of the bulk diffusion coefficients.

$$\frac{d^2 \varphi_B}{d\eta^2} = - L^2 \frac{k_1 K_A RT}{D_B(1+K_A p_0)} \frac{K_A p_0}{(1+K_A p_0)} \frac{(\alpha_1 - \frac{2D_B}{D_A} \varphi_B - \frac{D_D}{D_A} \varphi_D)^2}{(1 + \gamma_1 \varphi_B + \delta_1 \varphi_D)^2} \qquad (3a)$$

$$\frac{d^2 \varphi_D}{d\eta^2} = - L^2 \frac{k_2 K_A RT}{D_D(1+K_A p_0)} \frac{(\alpha_1 - \frac{2D_B}{D_A} \varphi_B - \frac{D_D}{D_A} \varphi_D)}{(1 + \gamma_1 \varphi_B + \delta_1 \varphi_D)} \qquad (3b)$$

where $\alpha_1 = 1.0$ \qquad (4a)

$$\gamma_1 = \frac{K_A p_0}{1+K_A p_0} \left(\frac{K_B}{K_A} - \frac{2D_B}{D_A} + \frac{K_C}{K_A} \frac{D_B}{D_C} \right) = -0.171 \qquad (4b)$$

$$\delta_1 = \frac{K_A p_0}{1+K_A p_0} \left(\frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{K_C}{K_A} \frac{D_D}{D_C} \right) = -0.331 \qquad (4c)$$

$$\omega_1 = 1.0 \qquad (4d)$$

Substituting these values in the above equations, the following are obtained.

$$\frac{d^2 \varphi_B}{d\eta^2} = - \frac{4.91 \times L^2 (1 - 1.46 \varphi_B - 1.375 \varphi_D)^2}{(1 - 0.171 \varphi_B - 0.331 \varphi_D)^2} \qquad (5a)$$

$$\frac{d^2 \varphi_D}{d\eta^2} = - \frac{0.323 \times L^2 (1 - 1.46 \varphi_B - 1.375 \varphi_D)}{(1 - 0.171 \varphi_B - 0.331 \varphi_D)} \qquad 5b)$$

$$S_D = \frac{0.076 \frac{d\varphi_B}{d\eta}\Big|_{\eta=0}}{2 \times 0.076 \frac{d\varphi_B}{d\eta}\Big|_{\eta=0} + 0.139 \frac{d\varphi_D}{d\eta}\Big|_{\eta=0}}$$

$$S_o = \frac{K_2 \, K_A p_o}{1 + K_A p_o (1 + 2 \, K_2)} = 0.471$$

and $\quad S_R = S_D / 0.471$

The values of selectivity ratio is obtained by solving equation 5a and 5b with the following boundary conditions:

$$\varphi_B(o) = \varphi_D(o) = 0$$

$$\frac{d\varphi_B}{d\eta}\bigg|_{\eta=1} = \frac{d\varphi_D}{d\eta}\bigg|_{\eta=1} = 0$$

and for different lengths of the pore, L, The results are summarized in the table below:

L Cm.	φ_M	S_R
0.1	.226	.998
0.2	.452	.995
0.5	1.33	.980
1.0	2.66	.959

...